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(54) 【発明の名称】 インク組成物

(57) 【要約】

【課題】 使用されるプリンタの保守特性が良好で、光学密度及び印刷特性に優れる、インクジェット・プリンタ用インク組成物を提供する。

【解決手段】 水性インク組成物は、水性キャリア、不溶性顔料、重合体分散剤からなる第1成分、ならびに、1, 3-プロパンジオールまたは1, 4-ブタンジオールと、ポリエチレングリコール型材料及びポリオールと酸化アルキレンとの縮合生成物から選択された第2の成分からなる特定の補助助溶媒混合物によって構成される。

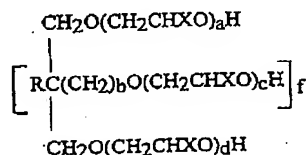
【特許請求の範囲】

(a) 約1重量%～約10重量%の顔料、
(b) 約0.1重量%～約10重量%の上記顔料用の重合体分散剤、

(c) 約50重量%～約93重量%の水性キャリア、ならびに

(d) (1) 1, 3-プロパンジオール又は1, 4-ブタンジオール、及び(2)下記の(i)～(iii)の群から選ばれる物質とを含み、該(1)と(2)の重量比(1):(2)が、約70:30～約30:70である、約5重量%～約40重量%の補助溶媒混合物、とを含む、インクジェット・プリンタの使用に適した水性インク組成物。(i) 約200～約3,400の分子量を有するポリエチレングリコール類、ならびにポリエチレングリコール類とポリプロピレングリコール類との混合物、(ii) 下記の式を有するポリオールと酸化アルキレンの縮合生成物、

【化1】



式中、XはH又はCH₃、RはH、C₁～C₄のアルキル基、又はCH₂O(CH₂CH₂O)_eH、bは0又は1、a+d+f(c+e)は約2～約100、fは約1～約6である、(iii)これらの混合物。

【請求項2】 前記補助溶媒混合物が、

(1) 1, 3-プロパンジオール又は1, 4-ブタンジオール、ならびに

(2) 下記の(i)～(iii)の群から選ばれる物質、を含むことを特徴とする、請求項1に記載のインク組成物。

(i) 約200～約3,400の分子量を有するポリエチレングリコール、(ii) 上記ポリオールと酸化アルキレンの縮合生成物であって、式中、Xが水素、Rが水素、bが0、fが1、a+d+f(c+e)が26であるもの、(iii)これらの混合物。

【請求項3】 前記補助溶媒混合物の約10重量%～約20重量%を含有することを特徴とする、請求項2に記載のインク組成物。

【請求項4】 前記補助溶媒混合物において、ポリエチレングリコール成分(i)が、約400の分子量を有するポリエチレングリコールであることを特徴とする、請求項3に記載のインク組成物。

【請求項5】 前記補助溶媒混合物が、1, 3-プロパンジオールと約400の分子量を有するポリエチレングリコールとの混合物であることを特徴とする、請求項4に記載のインク組成物。

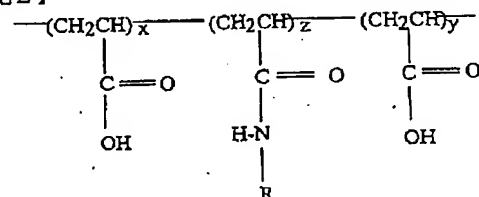
【請求項6】 前記(1)と(2)の重量比(1):(2)が、約50:50であることを特徴とする、請求項4に記載のインク組成物。

ンク組成物。

【請求項7】 前記重合体分散剤が、下記の(a)～(d)からなる群から選択される構造単位を主鎖に含むことを特徴とする、請求項1に記載のインク組成物。

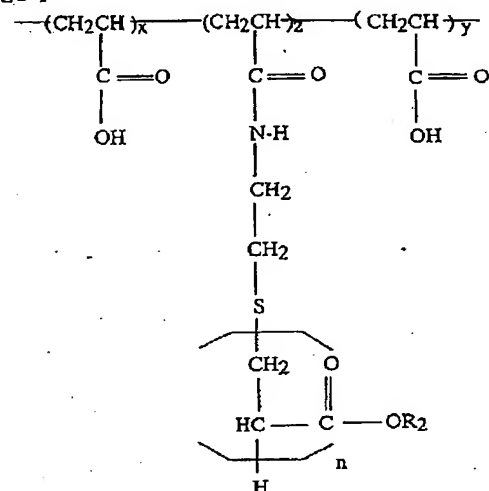
(a)

【化2】



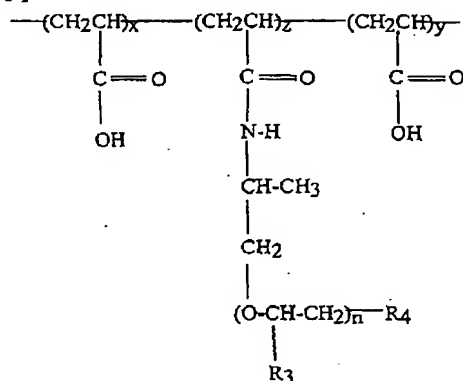
式中、x+yは約20～約200、zは約1～約10、RはC₆～C₃₆のアルキル基又はR₁、R₁はC₄～C₂₀のアルキル基である、(b)

【化3】



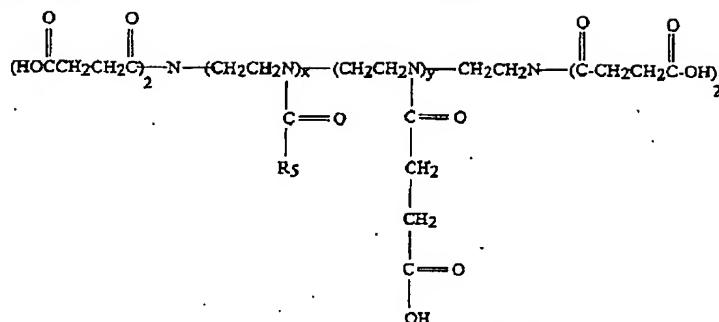
式中、x+yは約20～約200、zは約1～約10、nは約2～約40、R₂はアルキル基又はアリール基である、(c)

【化4】

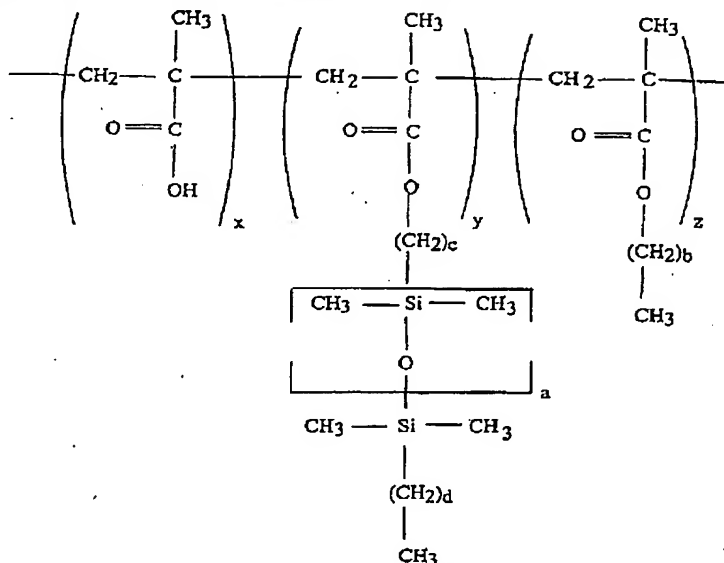


式中、x+yは約20～約200、zは約1～約10、R₃はH又はCH₃、R₄はH、CH₃又はOCH₃、

【化5】



【化6】



【請求項13】 前記補助溶媒混合物が、
(1) 1, 3-プロパンジオール又は1, 4-ブタンジオール、ならびに

(2) 下記の(i)~(iii)からなる群から選択された物質、とを含むことを特徴とする、請求項11に記載のインク組成物。

(i) 約200~約3,400の分子量を有するポリエチレングリコール、(ii) 前記ポリオールと酸化アルキレンとの縮合生成物で、Xは水素、Rは水素、bは0、fは1、 $a+d+f(c+e)$ は26であるもの、(iii) これらの混合物。

【請求項14】 上記補助溶媒混合物の約10重量%~約20重量%を含有することを特徴とする、請求項13に記載のインク組成物。

【請求項15】 前記補助溶媒混合物が、

(1) 1,3-プロパンジオール、ならびに

(2) 下記の(i)~(iii)からなる群から選択した物質、とを含むことを特徴とする、請求項14に記載のインク組成物。

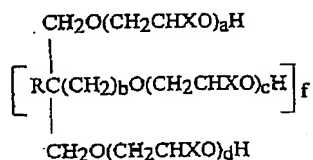
(i) 約400の分子量を有するポリエチレングリコール、(ii) 前記ポリオールと酸化アルキレンとの縮合生成物で、Xは水素、Rは水素、bは0、fは1、 $a+d+f(c+e)$ は26であるもの、(iii) これらの混合物。

【請求項16】 前記(1)と(2)の重量比(1):(2)が、約50:50であることを特徴とする、請求項15に記載のインク組成物。

【請求項17】 前記水性キャリアが、水；又は、1,5-ペンタンジオール、1,6-ヘキサンジオール、1,7-ヘプタンジオール、n-プロパノール、及びこれらの混合物からなる群から選択された有機溶媒と水との混合物；であり、水約50重量%/有機溶媒約50重量%~水約99.9重量%/有機溶媒約0.1重量%を含むことを特徴とする、請求項16に記載のインク組成物。

【請求項18】 (1) 1,3-プロパンジオール又は1,4-ブタンジオール、ならびに、(2) 下記の(i)~(ii)の群から選ばれる物質とを含み、該(1)と(2)の重量比(1):(2)が、約70:30~約30:70である補助溶媒混合物。(i) 約200~約3,400の分子量を有するポリエチレングリコール類、ならびにポリエチレングリコール類とポリプロピレングリコール類との混合物、(ii) 下記の式を有するポリオールと酸化アルキレンの縮合生成物、

【化7】



式中、XはH又はCH₃、RはH、C1~C4のアルキル基、又はCH₂O(CH₂CH₂O)_eH、bは0又

は1、 $a+d+f(c+e)$ は約2~約100、fは約1~約6である、(iii) これらの混合物。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明はインクジェット・プリンタに使用するインク組成物に関する。

【0002】

【従来の技術】 インクジェット印刷は、インクをノズルから紙又は他の印刷媒体に噴射することにより行われる。インクは媒体に向けて、各種の方法により噴射させることができる。例えば、静電印刷では、インクはノズルから媒体に向けて静電場により噴射される。スクイーズ・チューブとして知られる他のインクジェット印刷の手順では、インク・ノズル中に圧電素子を使用している。圧電素子の電気的歪みにより、インクがノズルを通して印刷媒体に移送される。サーマル又はバブル・インクジェット印刷として知られる他のインクジェット印刷の手順では、ノズル内で気相のバブルが膨張することにより、インクがノズルから印刷媒体に向けて噴射される。これら各種の印刷法については、ダーベック (Durbek) 及びシャー (Sherr) 編「ハード・コピー出力装置 (Output Hard Copy Devices)」、アカデミック・プレス (Academic Press) 1988年発行 (特に第13章「インクジェット印刷 (Ink Jet Printing)」参照) に記載されている。

【0003】 インクジェット・プリンタに使用するインク組成物は通常、脱イオン水、水溶性又は水と相溶性の有機溶媒、及び着色剤を含む。一般に、着色剤は可溶性の染料である。残念なことに、可溶性染料を含むインクには、耐水性が低い、耐光性が良くない、溶媒の蒸発や染料の溶解度の変化により噴射チャネル中に詰まりが生じる、染料が結晶する、インクのにじみやフェザリングなどを含めて印刷品質がよくない、熱安定性が低い、耐化学薬品性が低い、酸化しやすいなどの多くの問題がある。

【0004】 これらの問題の多くは、インク処方に使用する可溶性染料の代わりに不溶性の顔料を使用することにより解決することができる。一般に、顔料は染料と比較して特性が優れており、特に耐水性、耐光性、熱安定性、酸化安定性、及びコーティング又は処理した紙にも普通紙にも適合できるなどの点で優れている。しかし、顔料はインク組成物に溶解せず、したがって分散させる必要があるため、いくつかの新たな問題が生じる。インクの安定性は、特性の均一性を維持すること、ならびに、使用しない間に顔料がインクジェットに詰まらないようにすることの両方の点において、極めて重要である。安定性とコストの両方の理由から、もちろんインク組成物中に必要な顔料の量を最少限にするのが理想的である。しかし、インク組成物中の顔料の量を減らすと、画像の光学密度が低下する。さらに、必要な安定性を確

保するために組成のバランスが必要で、そのため、組成物をインクジェット・プリンタに使用するには適切な粘度を有するとともに、耐水性、耐光性が良好で、紙に印刷した場合にランニングやフェザリングが最少であることも重要である。これまで、これらの特性をすべて最適化したインク処方を開発することは非常に困難であった。一般的な方法としては、相反することが多いこれらの特性のバランスをとり、最適化することを目的として、インク組成物の分散剤と溶媒系を調節することが行われていた。しかし、本発明以前に特定の重合体分散剤を使用せずにこれらすべての特性を最適化した処方では達成されていなかった。

【0005】1993年1月19日付の、マトリック(Matrick)らの米国特許第5,180,425号明細書には、水性キャリア媒体、顔料分散液、及びポリオールと酸化アルキレンの補助溶媒を含むインクジェット用インク組成物が記載されている。これらのインクには、インクジェット・プリンタ機能の寿命を長くし、耐皮膜形成性があることが教示されている。ライボニック(Liponic)EG-1が、開示された好ましい補助溶媒のひとつである。この特許に使用する他の溶媒には、ポリエチレングリコールが含まれている。

【0006】1994年4月12日付の、ウィックラマナイケ(Wickramanayke)の米国特許第5,302,197号明細書には、顔料分散液、水性キャリア媒体、及びポリオールと酸化アルキレンの縮合生成物と環状アミド誘導体を含む補助溶媒混合物を含むインクジェット用のインク組成物が記載されている。ライボニックEG-1が、ポリオールと酸化アルキレンの縮合生成物成分として有用であることが教示されている。

【0007】1994年6月29日付の、チャン(Chan)らの欧州特許第603,469号出願には、水性キャリア媒体、特定のアルキルポリオールエーテル補助溶媒、及び顔料分散液(分散剤により顔料粒子を安定化したもの)からなるインクジェット用インクが記載されている。これらのインクは、粘度、表面張力、ノズルの詰まり防止、印刷品質、光安定性、耐にじみ性及び耐水性のバランスが良好であると教示されている。開示の発明で使用する溶媒には、1,2,3-ブタントリオールが含まれる。

【0008】1986年7月1日付の、オータらの米国特許第4,597,794号明細書には、鮮明な像を形成し、良好な物理特性を有するといわれるインクジェット印刷プロセスに使用するインク処方が記載されている。このインクに使用するために特に開示された溶媒には、ポリエチレングリコールと1,2,6-ヘキサントリオールが含まれる。

【0009】1,3-プロパンジオール又は1,4-ブタンジオールを、(a)低分子量のポリエチレングリコールもしくは関連する化合物、又は(b)ポリオールと

酸化アルキレンの縮合生成物のいずれかと共に含有する特定の補助溶媒混合物を、不溶性顔料の分散液を含有する水性インク組成物に使用することにより、特性を最適化する上で特徴的な混合を与えることが見出された。すなわち、これらの組成物は安定性、光学密度(低い顔料濃度を用いた場合でさえ)、粘度、印刷特性(耐水性、耐光性、印刷されたページにおけるフェザリング及びインクのランニングが最小)、ならびにプリンタ保守の問題(プリンタ不使用時のプリンタ・ジェットの目詰まりが最小)などの点において、優れた特性が得られる。上記の特許にはいずれも、本発明で示す特定の補助溶媒の組み合わせについては記載も示唆もない。

【0010】

【発明が解決しようとする課題】したがって、本発明の目的は、特定の補助溶媒系を含むインクジェット・プリンタ用の改善された顔料インク組成物を提供することにある。

【0011】

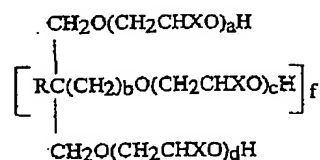
【課題を解決するための手段】本発明の他の目的及び特徴は、下記の開示により明らかとなる。

【0012】本発明の第1の態様では、

- (a)約1重量%～約10重量%の顔料、
- (b)約0.1重量%～約10重量%の上記顔料用の重合体分散剤、
- (c)約50重量%～約93重量%の水性キャリア、及び
- (d)(1)1,3-プロパンジオール又は1,4-ブタンジオールと、(2)下記の(i)～(iii)の群から選ばれる物質とを含む約5%～約40%の補助溶媒混合物、とを含む、インクジェット・プリンタの使用に適した水性インク組成物が提供される。(i)約200～約3,400の分子量を有するポリエチレングリコール類、ならびにポリエチレングリコール類とポリプロピレングリコール類との混合物、(ii)下記の式を有するポリオールとポリ酸化アルキレンの縮合生成物。

【0013】

【化8】



【0014】式中、XはH又はCH₃、RはH、C₁～C₄のアルキル基、又はCH₂O(CH₂CH₂O)_eH、bは0又は1、a+d+f(c+e)は約2～約100、fは約1～約6である。(iii)これらの混合物。なお、上記(1):(2)の重量比(1):(2)は、約70:30～約30:70である。

【0015】本発明の第2の態様は、上記(d)で示した補助溶媒混合物に関する。

【0016】本明細書に使用した百分率及び比は、他に指定しない限り「重量%」及び「重量比」である。本明細書に使用した分子量は、他に指定しない限り数平均分子量である。

【0017】

【発明の実施の形態】本発明は、インクジェット・プリンタに使用するのに適した水性インク組成物に関する。これらの組成物は、不溶性顔料、顔料のための重合体分散剤（顔料と分散剤は分散液としての組成物中に存在する）、水性キャリア、及び特定の補助溶媒混合物を含有する。これら必要成分の各々は、いくつかの追加成分とともに、以下において詳細に説明する。

【0018】重合体分散剤は本発明の組成物において、最終成分の約0.1%～約10%、好ましくは約0.25%～約5%、最も好ましくは約0.5%～約4%含まれる。本発明で使用するのに適した重合体分散剤には、インクジェット用インク調製物の分散剤として使用するのに適することが業界で知られている陰イオン性、陽イオン性、非イオン性重合体のいずれもが含まれる。このような材料の例は、本明細書に参照として添付された1994年5月10日付の、ショア（Shor）らの米国特許第5,310,778号明細書に記載されている。このような重合体分散剤は、単独重合体でも、共重合体でも、分岐状重合体でも、グラフト重合体でもよい。また、ランダム重合体でもブロック重合体でもよい。

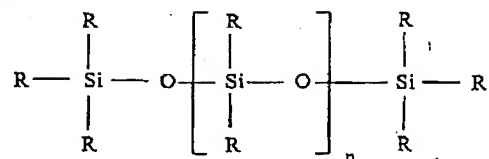
【0019】AB、BAB、及びABCのブロック共重合体は、本発明に有用な重合体分散剤の1種である。好ましいものは、少なくとも1種のアルキルアクリル又はメタクリル酸エステル及びアミン置換アクリル又はメタクリル酸エステルの単量体類から誘導されたAB、BAB、及びABCブロック共重合体である。好ましいAB及びBABブロック共重合体と、これらの製法は、本明細書に参照として添付された1992年2月4日付の、マー（Ma）らの米国特許第5,085,698号明細書に記載されている。

【0020】本発明の実施に有用な重合体分散剤は、通常、疎水性と親水性の重合体セグメントの両方を含み、疎水性セグメントはインク組成物中の顔料粒子と結合する傾向があり、親水性セグメントは液体インク媒体により溶媒和する傾向があり、これらと立体的機構及び／又はイオン性機構により分散液を安定化させる。

【0021】本発明で使用する好ましい種類の重合体分散剤は、親水性重合体セグメントと加水分解に対して安定なシロキシル置換基を含む疎水性重合体セグメントとを含むブロック又はグラフト共重合体を含む。これらの分散剤の組のうち特に好ましいものは、親水性重合体セグメント（特に、アクリレート又はメタアクリレート共重合体）と、下記の式を有する高分子体から誘導された疎水性重合体セグメントとを含むグラフト共重合体である。

【0022】

【化9】



【0023】式中、nは2～16、Rはそれぞれ独立した低級アルキル（C1～C6）又はシロキシルである。これらの材料は、本明細書に参照として添付された1994年12月21日付、ビーチ（Beach）らの米国特許出願第08/360,199号明細書に開示されている。

【0024】他の種類の好ましい重合性分散剤は、約1,500～約20,000の分子量を有し、(a)親水性重合体セグメント、(b)加水分解に対して安定なシロキシル置換基を有し、約400～約3,000の分子量を有する疎水性重合体セグメント、ならびに(c)反応性の界面活性高分子体、保護コロイド高分子体、及び非シロキシル疎水性単量体からなる群から選択された安定化セグメント、とを含むグラフト共重合体である。

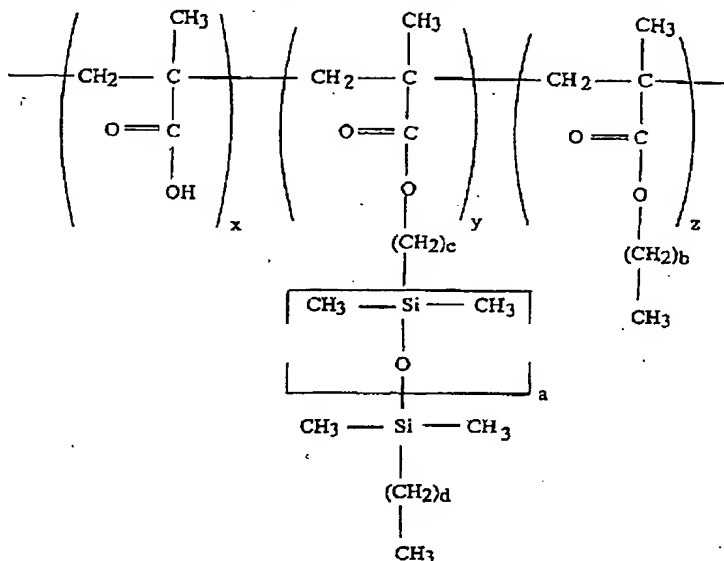
【0025】好ましい単量体比(a):(b)は約10:1～約100:1であり、好ましい単量体比

(b):(c)は約1:0.5～約1:5である。好ましい親水性重合体セグメントはカルボキシ置換基を含むもので、アクリレート又はメタクリレート重合体物質が最も好ましい。好ましいシロキサン含有疎水性重合体セグメントは、末端にアクリロイル又はメタクリロイル基を有するポリジアルキルシロキサン高分子体である。最も好ましい疎水性セグメントは約400～約2,000の分子量を有し、ジメチルポリシロキシ基を有するものである。好ましい安定化セグメントは、ステアリルアクリレート、ステアリルメタクリレート、ラウリルアクリレート、ラウリルメタクリレート、ノニルフェノールアクリレート、ノニルフェノールメタクリレート、nが約1～約40であるノニルフェノキシポリ（エチレンオキシ）nメタクリレート；nが約1～約40であるノニルフェノキシポリ（エチレンオキシ）nアクリレート；nが約5～約40であるメトキシポリ（エチレンオキシ）nメタクリレート；nが約5～約40であるメトキシポリ（エチレンオキシ）nアクリレート；nが約1～約20であるステアリルオキシポリ（エチレンオキシ）nメタクリレート；nが約1～約20であるステアリルオキシポリ（エチレンオキシ）nアクリレート；フッ素化C1～C18アルキルメタクリレート；フッ素化C1～C18アルキルアクリレート；ポリ（プロピレングリコール）メチルエーテルメタクリレート；ポリ（プロピレングリコール）メチルエーテルアクリレート、ポリ（プロピレングリコール）4-ノニルフェニル

これらの混合物を含む。

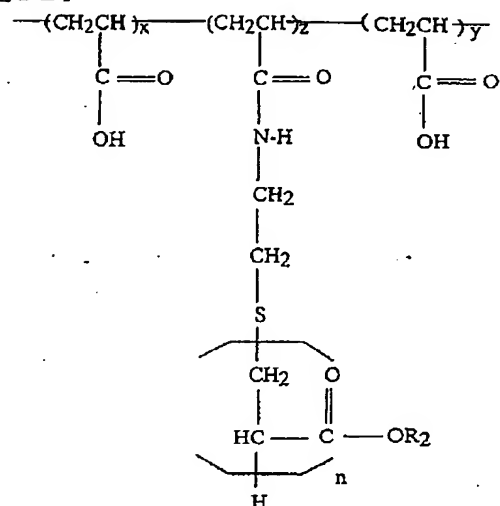
【0027】

【化10】


$$\begin{array}{ccccc} \text{---}(\text{CH}_2\text{CH})_x\text{---} & \text{---}(\text{CH}_2\text{CH})_z\text{---} & \text{---}(\text{CH}_2\text{CH})_y\text{---} \\ | & | & | \\ \text{C=O} & \text{C=O} & \text{C=O} \\ | & | & | \\ \text{OH} & \text{H-N} & \text{OH} \\ & | & \\ & \text{R} & \end{array}$$

【0032】

【化12】



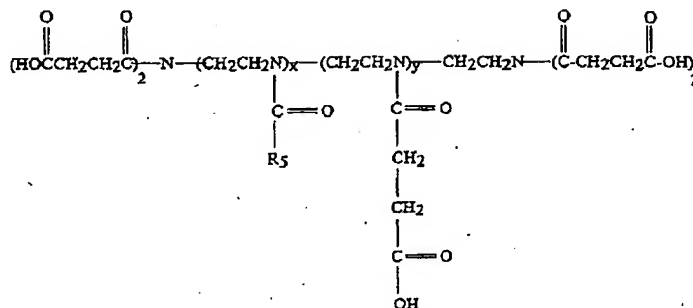
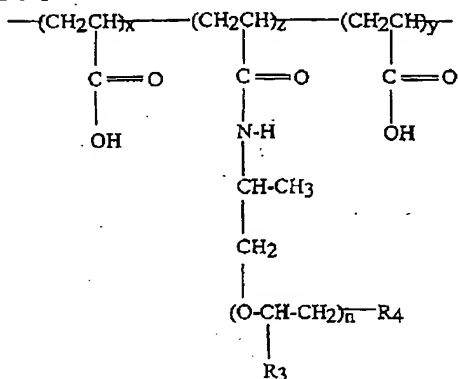
【0030】

【化1 1】

【0033】式中、 $x+y$ は約20～約200、 z は約1～約10、 n は約2～約40、 R_2 はアルキル基又はアリール基、好ましくはブチル基、又は

【0034】

【化13】



【0037】式中、 y は約6～約20、 x は約1～約5、 R_5 はC6～C30のアルキル基である。

【0038】本発明のグラフト共重合体分散剤は、粒子の安定性を得るために比較的分子量であり、安定なインクジェット印刷用インクに使用するために粘度が低い必要がある。このため、共重合体を生成するための極性溶媒重合法が選択される。このような方法により、得られる共重合体だけでなく、すべての出発原料（フリー・ラジカル開始剤、疎水性及び親水性単量体、ならびに連鎖移動剤）の溶解性を維持することにより、共重合体の分子量と均一性が制御される。合成された共重合体は、インクジェット印刷用に処方するために、水性媒体に懸濁させる必要があるため、反応混合物中の極性有機溶媒から共重合体を回収し、水に溶解させる必要がある。代表的な極性重合溶媒からの共重合体回収方法は、以下の工程を含む。

1. 共重合体の溶液をヘキサンなどの非溶媒に添加して、溶液から重合体を沈殿させ、これにより共重合体を精製し、
2. 沈殿物を真空ろ過し、
3. 共重合体沈殿物を乾燥する。

【0039】次に共重合体粉末を水性塩基に溶解して、インクジェット印刷用インクの生成に使用することがで

【0035】式中、 $x+y$ は約20～約200、 z は約1～約10、 R_3 はH又はCH₃、 R_4 はH、CH₃、又はOCH₃、 n は約10～約60、もしくは下記の式を有するものである。

【0036】

【化14】

きる。この方法はコストが高く、不必要に複雑である。

【0040】極性有機重合溶媒から共重合体の分散剤を回収するための好ましい方法は、共重合体の分散剤をただ回収するだけでなく、これらの分散剤から生成されるインクジェットインクがサテライトやスプラックを形成するのを減少させるような、印刷品質を改善するものである。具体的には、これらの好ましい方法は下記の工程を含む。

1. 溶媒を蒸発させた後、水性塩基に溶解し、
2. 溶媒を交換する。

【0041】溶媒蒸発及び溶解工程では、真空トレイ乾燥、回転蒸発乾燥、ドラム乾燥、回転円筒真空乾燥、又は噴霧乾燥など、共重合体の溶液を乾燥粉末に変換する標準的な方法により、極性溶媒を最初に共重合体から蒸発させる。次に、乾燥した共重合体粉末を水性塩基に溶解して、インクジェット用の顔料のインクの生成に使用できるようにする。

【0042】溶媒交換法工程では、重合反応器中の極性溶媒の約35%～約60%（好ましくは約50%）を蒸留により除去し、脱イオン水と水性塩基（例えば、KOH溶液）を加えてpHを約4.5～約6.5、好ましくは約5に調節する。沸点が水より低い極性溶媒の場合は、温度が全ての極性溶媒が除去される約100℃に達

するまで、溶媒を蒸留させるためにこの混合物の温度をゆっくり上昇させる。(この工程は、極性溶媒の沸点が水の沸点より高い場合には用いることができない。)さらに水性塩基(例えば、KOH溶液)をこの溶液に加えて、pHを約7〜約8.5、好ましくは約7.5に上昇させる。次いで、この溶液はインクジェット用の顔料インクの処方に使用される。

【0043】本発明のインク組成物の第2の成分は、不溶性の着色剤である顔料である。本発明の組成物には、顔料が最終組成物に対して、約0.1%〜約10%、好ましくは約0.25%〜約5%、最も好ましくは約0.5%〜4%存在する。実際に、本発明の重要な利点の一つは、低い顔料濃度(例えば0.5〜4%)を有するインクの処方を可能にし、しかも高品質で、優れた光学密度を提供することである。本発明の実施に有用な顔料としては、本明細書に参照として添付された1992年2月4日付、マー(Ma)らの米国特許第5,085,698号明細書に開示されているような、当業界で周知の従来の顔料のいずれをも使用することができる。顔料は単独で使用しても、組み合わせて使用してもよい。

【0044】顔料の粒子は、インクがインクジェット印刷装置、特に直径が通常約10 μ m〜約50 μ mである噴射ノズル中を自由に流動することができるように、十分小さい必要がある。粒径はまた、インクの寿命を通じて重要である顔料の分散安定性に影響を与える。微粒子のブラウン運動が粒子の凝集防止に役立ち、これにより製品をさらに安定化させる。有用な粒径範囲は、約0.05 μ m〜約15 μ mである。好ましくは、顔料の粒径は約0.05 μ m〜約5 μ mの範囲であり、最も好ましくは、約0.05 μ m〜約1 μ mの範囲である。顔料は乾燥した形態でも湿潤した形態でも使用することができる。例えば、顔料は通常水性媒体中で製造され、水を含んだプレスケーキとして得られる。このプレスケーキの形態では、顔料は乾燥形態の場合のように凝集しない。したがって、水を含んだプレスケーキの形態の顔料は、乾燥した顔料を使用した場合のようにインクの製造工程において解凝集を行う必要がない。

【0045】金属又は金属酸化物の微粒子も本発明の実施に使用することができる。例えば、金属及び金属酸化物は、磁気インクジェット用インクの製造に適している。微粒子の酸化物、例えば、シリカ、アルミナ、チタニアなどもまた使用することができる。さらに、微粉碎した金属粒子、例えば、銅、鉄、鋼、アルミニウム、及び合金類は、適切な用途のために選択することができる。

【0046】本発明の実施に使用することのできる顔料の例には、アゾ・レーキ、縮合アゾ顔料、キレートアゾ顔料などのアゾ顔料；フタロシアニン顔料、ペリレン顔料、アントラキノン顔料、キナクリドン顔料、ジオキサジン顔料、チオインディゴ顔料、イソインドリノン顔

料、キノフタロン顔料などの多環式顔料；塩基性染料レーキ、酸性染料レーキなどの染料レーキ；ニトロ顔料、ニトロソ顔料、アニリンブラック、デライト蛍光顔料などの有機顔料；酸化チタン、酸化鉄、カーボンブラックなどの無機顔料などがある。本発明において使用するのに好ましい顔料は、酸化チタン、酸化鉄及びカーボンブラックを含む。本発明において使用することのできる市販の入手可能な顔料の例には、商標名HeliogenブルーL 6901F(BASF)、商標名HeliogenブルーNBD 7010(BASF)、商標名HeliogenブルーK 7090(BASF)、商標名HeucophthalブルーGBT-583D(ヒューバック)、商標名Irgaliteルビン4BL(チバ・ガイギー)、商標名Quindoマゼンタ(モベイ)、商標名Indofastブリリアント・スカーレット(モベイ)、商標名HostapermスカーレットGO(ヘキスト)、パーマネント・ルビンF6B(ヘキスト)、商標名Monastralスカーレット(チバ・ガイギー)、商標名Raven1170(コル・ケム)、スペシャル・ブラック4A(デグサ)、ブラックFW18(デグサ)、商標名SterlingNSブラック(キャボット)、商標名SterlingNSX76(キャボット)、Monarch880(キャボット)、商標名TipureR-101(デュボン)、モガルL(キャボット)、BK8200(ボール・ウーリッチ)、商標名HeliogenグリーンK 8683(BASF)、商標名HeliogenグリーンL9140(BASF)、商標名MonastralレッドB(チバ・ガイギー)、商標名MonastralバイオレットR(チバ・ガイギー)、商標名HostapermオレンジGR(ヘキスト)、商標名Paliogenオレンジ(BASF)、L75-2377イエロー(サン・ケム)、L74-1357イエロー(サン・ケム)、商標名HostapermイエローH4G(ヘキスト)、商標名Argazinイエロー5GT(チバ・ガイギー)、パーマネントイエローG3R-01(ヘキスト)、商標名NovopermイエローFGL(ヘキスト)、商標名Chromophthalイエロー3G(チバ・ガイギー)、ハンザイエローX(ヘキスト)、商標名DalamarイエローYT-858-D(ヒューバック)、ハンザブリリアントイエロー5GX-02(ヘキスト)などがある。

【0047】本発明のインク組成物の第3の成分は、水性キャリア媒体である。この成分は、水(好ましくは脱イオン水)又は水と少なくとも1種類の水溶性有機溶媒の混合物である。水性キャリア成分は、本発明の組成物の約50%〜約93%、好ましくは約70%〜約80%存在する。適当な混合物の選択は、処方される特定のイ

シクの要件、例えば、望ましい表面張力及び粘度、使用する顔料、顔料インクに必要な乾燥時間、ならびにインクが印刷される紙の種類などに依存する。選択することができる水溶性有機溶媒の代表例としては、(1)メチルアルコール、エチルアルコール、n-プロピルアルコール、イソプロピルアルコール、n-ブチルアルコール、sec-ブチルアルコール、t-ブチルアルコール、イソブチルアルコール、フルフリルアルコール、テトラヒドロフルフリルアルコールなどのアルコール類；(2)アセトン、メチルエチルケトン、ジアセトンアルコールなどのケトン類又はケトアルコール類；(3)テトラヒドロフラン、ジオキサンなどのエーテル類；(4)酢酸エチル、乳酸エチル、炭酸エチレン、炭酸プロピレンなどのエステル類；(5)エチレングリコール、ジエチレングリコール、グリセロール、2-メチル-2, 4-ペンタンジオール、1, 2, 6-ヘキサントリオール、チオジグリコールなどの多価アルコール類；(6)エチレングリコールモノメチル(又はモノエチル)エーテル、ジエチレングリコールモノメチル(又はモノエチル)エーテル、プロピレングリコールモノメチル(又はモノエチル)エーテル、トリエチレングリコールモノメチル(又はモノエチル)エーテル、ジエチレングリコールジメチル(又はジエチル)エーテルなどのアルキレングリコール類から誘導された低級アルキルモノ又はジエーテル類；(7)ピロリドン、N-メチル-2-ピロリドン、1, 3-ジメチル-2-イミダゾリジノンなどの窒素含有環状化合物、(8)ジメチルスルホキシド、テトラメチルスルホンなどのイオウ含有化合物がある。他の有用な溶媒には、ラクトン類及びラクタム類がある。

【0048】本発明でキャリア媒体として水と有機溶媒の混合物を使用する場合、媒体は通常、水約25%/有機溶媒約75%〜水約99.9%/有機溶媒約0.1%を含有する。好ましい比は、水約50%/有機溶媒約50%〜水約99.9%/有機溶媒約0.1%である。これらの百分率は、水性キャリア媒体の全重量に対するものである。本明細書で使用する「有機溶媒」の用語で、水性キャリア媒体に使用されるものは、本発明の補助溶媒の成分として使用される特定の材料を含むことを意図するものでないことを理解されたい。

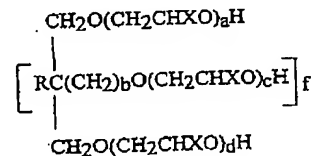
【0049】本発明の水性キャリア媒体成分に使用する好ましい有機溶媒には、エチレングリコール、1, 2, 6-ヘキサントリオール、チオジグリコール、ヘキシレングリコール、ジエチレングリコールなどの多価アルコール類；ペンタンジオール、ヘキサンジオール、同族列ジオール類などのジオール類；ラウリン酸プロピレングリコールなどのグリコールエーテル類；グリセロール；及びエチレングリコールモノメチル(又はモノエチル)エーテル、ジエチレングリコールメチル(又はエチル)エーテル、トリエチレングリコールモノメチル(又はモ

ノエチル)エーテル、などの多価アルコールの低級アルキルエーテル類；メタノール、エタノール、プロパノール、ブタノールなどのアルコール類；アセトンなどのケトン類；テトラヒドロフラン、ジオキサンなどのエーテル類；酢酸エチル、スルホラン類、N-メチルピロリドンなどのエステル類；γ-ブチロラクトンなどのラクトン類；2-ピロリドン、1-メチル-2-ピロリドンなどのラクタム類がある。有機溶媒はインク組成物に乾燥時間の短縮、ブリードの減少、浸透性の増大などの有用な特性を与えるが、一般に(本明細書に定義する補助溶媒物質とは異なり)光学密度、組成物の安定性、又は印刷品質を改善することはない。特に好ましい有機溶媒には、1, 5-ペンタンジオール、1, 6-ヘキサンジオール、1, 7-ヘプタンジオール、n-プロパノール、及びこれらの混合物がある。

【0050】本発明の組成物で使用するのに必要な最後の成分は、補助溶媒混合物で、最終組成物の約5%〜約40%、好ましくは約5%〜約30%、最も好ましくは約10%〜約20%を占める。この補助溶媒混合物は第一成分である1, 3-プロパンジオール、1, 4-ブタンジオール、又はこれらの物質の混合物を含有する。これらのうちでは1, 3-プロパンジオールが好ましい。さらに、第二成分であるポリエチレングリコール型化合物、ポリオールと酸化アルキレンの縮合生成物、又はこれらの化合物の混合物も含有する。この補助溶媒混合物に使用される第2の成分は、分子量が約200〜約3, 400、好ましくは約200〜約600の、ポリエチレングリコール、又はポリエチレングリコールとポリプロピレングリコールの混合物である。ポリエチレングリコール類(PEG)が好ましく、約400の分子量を有するポリエチレングリコールが特に好ましい。補助溶媒の第2の成分は、下記の式を有するポリオールと酸化アルキレンの縮合生成物であってもよい。

【0051】

【化15】



【0052】式中、xはH又はCH₃、RはH、C₁〜C₄のアルキル基、又は-CH₂O(CH₂CH₂O)_eH、bは0又は1、a+d+f(c+e)は約2〜約100、fは約1〜約6である。

【0053】本発明で有用なポリオールと酸化アルキレンの縮合生成物は、ポリオールと酸化アルキレンの反応生成物である。これらは、本明細書に参照として添付された1993年1月19日付、マトリック(Matrick)らの米国特許第5, 180, 425号明細書に記載され

ている。これらの化合物は通常、水に対する溶解度が25℃で少なくとも約4.5%（すなわち水100部に対して4.5部）である。これらの化合物に使用する酸化アルキレンは、酸化エチレンもしくは酸化プロピレン、又は両酸化物の混合物である。単一の酸化アルキレンとの反応により、オキシアルキル化の度が異なる化合物の混合物を生じるが、示された構造は一連の酸化アルキレン単位を含有する平均的な組成に基づくものである。酸化プロピレンと酸化エチレンのランダム及びブロック共重合体を使用することができる。酸化アルキレンと反応したポリオールは、3個以上の水酸基を有していてもよい。有用なトリオールはグリセロール、トリメチロールプロパン、及びトリメチロールエタンである。1, 2, 4-ブタントリオールや1, 2, 6-ヘキサントリオールなどの他のトリオール類も使用することができ

る。有用なテトラオール類には、ペンタエリトリール、ジ(トリメチロールプロパン)、メチルグルコシドなどがある。グルコース、ペンツール、なども使用できる。ソルビツールは有用なヘキソールである。他の有用なヘキソール類には、ジペンタエリトリール及びイノシツールがある。ジオール類は、酸化アルキレンとの縮合生成物が通常、顔料分散液に適合しないので、本発明で使用するには一般に適当ではない。その例外のひとつはネオペンチルグリコールの酸化アルキレンとの縮合生成物である。

【0054】ポリオールと酸化アルキレンとの縮合生成物の例には下記のものがある。

【0055】

【表1】

表1

製品	R	a + d + f (c + e)	b	f
商標名 Liponic EG-1 ¹⁾	-H	26	0	1
商標名 Liponic SO-20 ¹⁾	-H	20	0	4
商標名 Photonol PHO-7149 ²⁾	-C ₂ H ₅	2.7	1	1
商標名 Photonol PHO-7155 ²⁾	-C ₂ H ₅	7.4	1	1
商標名 Voranol 230-660 ³⁾	-CH ₃	3.0	1	1
商標名 Voranol 234-630 ³⁾	-C ₂ H ₅	8.0	1	1
商標名 Fomrez T-279 ⁴⁾	-C ₂ H ₅	8.1	1	1
商標名 Fomrez T-315 ⁴⁾	-C ₂ H ₅	4.1	1	1

¹⁾ リボ・ケミカルズ・カンパニー、バターソン、N. J.

²⁾ ヘンケル・コーポレーション、アンブラー、P. A.

³⁾ ダウ・ケミカル・カンパニー、ミッドランド、M. I.

⁴⁾ ウィットコ・コーポレーション・オーガニック・デヴィジョン、ニューヨーク、N. Y.

【0056】本発明で使用するのに特に好ましいポリオールと酸化アルキレンとの縮合生成物は、上記のLiponic EG-1である。この材料はグリセレス-26のCTFAの名称を有し、グリセリンに26モルの酸化エチレンを付加したもので、リボ・ケミカルズ・カンパニー、バターソン、ニュージャージーから市販されて

いる。

【0057】補助溶媒混合物の第一及び第二成分は、約70:30～約30:70の重量比（第一成分：第二成分）で存在する。補助溶媒混合物がポリエチレングリコール（PEG）型の化合物と、1, 3-プロパンジオール又は1, 4-ブタンジオールのいずれかを含有する場

合は、最適なPEG：ジオールの重量比は約50：50～約70：30である。補助溶媒混合物がポリオールと酸化アルキレンとの縮合生成物を1，3-プロパンジオール又は1，4-ブタンジオールとともに含有する場合は、最適な縮合生成物：ジオール比は約30：70～約50：50である。一般に、最も好ましい助溶媒混合物の比は、約50：50である。

【0058】本発明のインク組成物は、このような組成物を製造するために当業界で知られているどのような方法によって調製してもよい。この組成物の重要な点は、顔料と重合体分散剤が、水性キャリアと補助溶剤混合物中で安定な分散液を形成することである。ひとつの方法では、最初に顔料と重合体分散剤を混合する。次に、得られたミルベースを磨砕機によって磨砕して粒子を許容粒径に減少させる。次にこの材料を他のインク成分及び水と混合して、所定の濃度のインクを得る。所望により界面活性剤を添加して顔料の分散を高め、インクの表面張力を変化させ、紙への浸透を制御することができる。好適な界面活性剤には、非イオン性、両性、及びイオン性界面活性剤がある。他の添加剤、例えば殺生剤、湿潤剤、キレート剤、粘度調整剤なども当業界で知られた利点を得るために、当業界で確立した使用濃度で、このインク組成物に添加することができる。

【0059】インクジェット用の顔料インクを生成する方法では、通常粉砕ロールを使って粒子の大きさを減少させることが必要である。インクの保存寿命は2年以上であることが望ましく、そして顔料の粒径については、このようなインクの保存寿命が得られるような粒径が選択されることが望ましい。このような粒径は、小さい粉砕媒体を使用して顔料粒子をせん断することにより得られる。顔料インクの調製に使用する代表的な媒体には、ステンレス・スチール、ケイ酸ジルコニウム、酸化ジルコニウム、及びガラスの球状粒子が含まれる。この粉砕工程で使用する表面積の大きい微粒子は、摩耗してイン

ク分散液中に混入し、最終処方を汚染することがある。この汚染は、種類と量にもよるが、インクの特性に悪影響を与えることがある。例えば、汚染により色顔料処方（特に黄色などの淡色）の変色、媒体が処方の化学薬品と反応することによるpHの変化、インクろ過の困難、及び印刷カートリッジの耐用寿命を通じてのインク機能の安定性低下などが生じることがある。好ましい粉砕媒体は、高度に平滑で均一な表面を有する高密度で高硬度の球状セラミック粒子である。本発明のインクの製造に使用するために特に好ましい粉砕媒体は、日本化学陶業が製造し、フィラデルフィアのSEファイアストーン・アソシエーツ（S.E. Firestone Associates）がY T Z セラミック・ビーズの名称で市販している材料である。この材料は、高純度の酸化ジルコニウムのコアをイットリウム処理して耐摩耗性を高めた球状のセラミック粒子である。この粒子は完全な球形で、きわめて平滑で均一な表面を有し、密度が6.0 g/cm³、硬度が91である。このような材料の製法の例については、本明細書に参照として添付された1982年11月25日公開の特開昭57-191234号明細書及び1981年11月11日公開の特開昭56-145118号明細書に記載されている。

【0060】

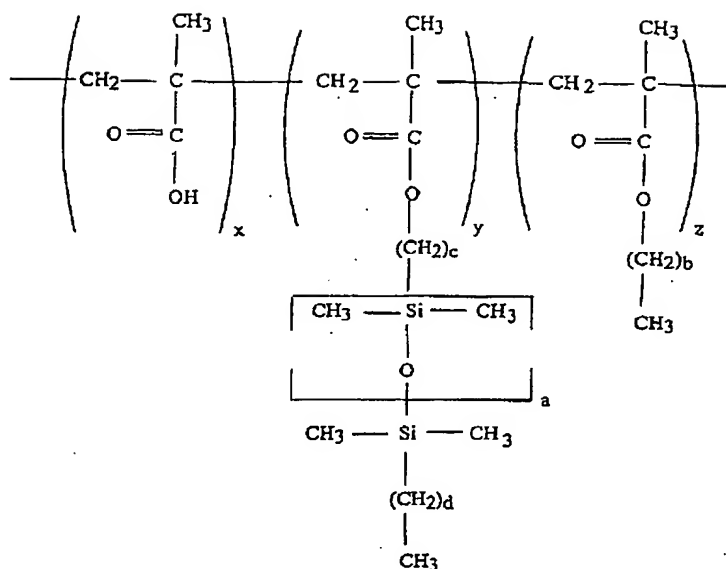
【実施例】下記の例は、本発明のインク組成物の製造及び使用法を詳細に示すものである。これらの詳細な説明は、上記の更に一般的な説明の範囲内にあり、これを例示するものである。これらの例は説明の目的のみであり、本発明の範囲を限定するものではない。

【0061】実施例1

本発明のインク組成物は、下記の一般式を有する重合体分散剤（以下、「三元共重合体L」と記す）を使用した。

【0062】

【化16】



【0063】(1) 三元共重合体Lの調製

三元共重合体Lは下記のようにして生成した。メタクリル酸22.8g(265ミリモル)、末端基にモノメタクリルオキシプロピル基を有するポリジメチルシロキサン(PDMS-MA)7.84g(8.7ミリモル、分子量900)、ステアリルメタクリレート2.95g(8.7ミリモル)、ドデカンチオール2.06g(9.9ミリモル)、ジメチル2,2'-アゾビスイソブチレート0.64g(2.84ミリモル)、及びイソプロピルアルコール100mlの溶液を、アルゴンで脱気(一部排気後ファイアストーン・バルブ[Firestone Valve]を使用してアルゴンを充填する工程を反復)した後、70℃で16時間加熱した。この混合物を室温に冷却した後、1.0リットルのヘキサンに高速で攪拌しな

がら徐々に添加した。得られた固体を減圧ろ過して分離し、真空中において80℃で一夜乾燥した。反応率は約85%であった。この共重合体の特性は、プロトンNMR及びGPCによって決定した。

【0064】分散剤の原液は、下記のようにして生成した。脱イオン水40gを入れた400mlビーカーを、マグネチック・スターラ付のホット・プレート上に載置した。三元共重合体L12gを攪拌しながらビーカー中に加えた後、20%KOH溶液18gをこれに加えた。この混合物を50℃で2時間加熱した。必要があれば、20%KOH溶液を添加してpHを7.5に調節した。次に脱イオン水を加えて上記の原液重量を100g(三元共重合体L12%)とした。

【0065】

(2) ミルベースの処方

(a) ミルベース処方A

成分	量
カーボンブラック(キャボット社、モナーク800)	26.0g
三元共重合体L原液	54.0g
脱イオン水	100.0g

(b) ミルベース処方B

成分	量
カーボンブラック (デグサ社、スペシャル・ブラック4A)	26.0g
三元共重合体L原液	54.0g
脱イオン水	100.0g

【0066】ミルベースA及びBは、下記のようにして処方した。成分をあらかじめ塊が見えなくなるまで機械的に攪拌することによって前混合した。この混合物を、10~12メッシュのケイ酸ジルコニウム・ショット付のシェグバリ(Szegvari)磨砕機モデル01std型で700rpmの速度で分散させた。この磨砕工程は、通常最低1時間行いが、温度を制御してこれより長時間行

うこともできる。得られた粉砕ミルベースを磨砕機から取り出し、脱イオン水を加えて最終固形分を12%にした。

【0067】ミルベース処方Aについて述べた分散液を使用して、下記の成分を有するインク組成物を調製した。

カーボンブラック	4% (重量)
三元共重合体L	1%
ポリエチレングリコール (分子量400)	10%
1, 3-プロパンジオール	10%
脱イオン水	75%

【0068】インク組成物は下記の手順で調製した。

(1) 脱イオン水、PEG、及び1, 3-プロパンジオールを20分間混合した。

(2) 粉碎したミルベース (ミルベース処方A) を攪拌しながら上記混合物に添加した。攪拌を20分間続けた。

(3) 20% KOH 溶液を加えて組成物のpHを8.3に調節した。

カーボンブラック	3%
三元共重合体L	0.75%
ポリエチレングリコール (分子量400)	14%
1, 3-プロパンジオール	6%
脱イオン水	76.25%

このインクをインクジェット・プリンタで使用し、代表的な6種類の異なる紙に印刷して試験した場合、良好な光学密度、良好な保守特性、及び高度の好ましい印刷特性を示した。

カーボンブラック	3%
三元共重合体L	0.75%
ポリエチレングリコール (分子量400)	10%
1, 3-プロパンジオール	10%
脱イオン水	76.25%

このインクを従来のインクジェット・プリンタで使した場合、良好な保守特性を示し、良好な光学密度とともに高度の好ましい一連の印刷特性を示す印刷物が得られた。

カーボンブラック	3%
三元共重合体L	1%
商標名Liponic EG-1	10%
1, 3-プロパンジオール	10%
脱イオン水	76%

このインクを従来のインクジェット・プリンタで使用する、良好な保守特性を示し、代表的な6種類の紙に印刷して試験した場合、(良好な光学密度を含む) 優れた印刷特性を示した。

カーボンブラック	3%
三元共重合体L	0.75%
1, 3-プロパンジオール	10%
ポリエチレングリコール (分子量400)	10%
脱イオン水	76.25%

このインクをインクジェット・プリンタで使用する、良好な保守特性を示し、代表的な6種類の紙に印刷して試験した場合、良好な光学密度を示した。

カーボンブラック
(FW18、デグサ社、リッジフィールドパーク、N. J.)

(4) 1. 2 μ mで濾過した。

【0069】このインクをインクジェット・プリンタで使用し、代表的な6種類の異なる紙に印刷して試験した場合、良好な保守特性、良好な光学密度、及び高度の好ましい印刷特性を示した。

【0070】実施例2

実施例1に記載のミルベース処方Bとその製法を用いて、下記の成分を有するインク組成物を調製した。

【0071】実施例3

実施例1に記載のミルベース処方Aとその製法を用いて、下記の成分を有するインク組成物を調製した。

【0072】実施例4

実施例1に記載のミルベース処方Bとその製法を用いて、下記の成分を有するインク組成物を調製した。

【0073】実施例5

実施例1に記載のミルベース処方Bとその製法を用いて、下記の成分を有するインク組成物を調製した。

【0074】実施例6

実施例1に記載の製法を用いて、下記の成分を有するインク組成物を調製した。

	3%
三元共重合体L	0.75%
1, 3-プロパンジオール	10%
ポリエチレングリコール(分子量400)	10%
脱イオン水	76.25%

このインクを従来のインクジェット・プリンタで使用する
と、良好な保守特性を示し、代表的な6種類の紙に印
刷して試験した場合、良好な光学密度を示した。

【0075】実施例7
実施例1に記載の製法を用いて、下記の成分を有するイ
ンク組成物を調製した。

カーボンブラック(FW18)	3%
三元共重合体L	0.75%
1, 3-プロパンジオール	10%
商標名Liponic EG-1	10%
商標名Kathon PFR (殺生剤、ローム&ハース)	0.15%
脱イオン水	76.10%

このインクを従来のインクジェット・プリンタで使用する
と、良好な保守特性を示し、代表的な6種類の紙に印
刷して試験した場合、良好な光学密度を示した。

【0076】実施例8
実施例1に記載の製法を用いて、下記の成分を有するイ
ンク組成物を調製した。

カーボンブラック(スペシャルブラック4A)	3%
三元共重合体L	0.75%
1, 4-ブタンジオール	10%
ポリエチレングリコール(分子量600)	10%
n-プロパノール	0.2%
脱イオン水	75%

このインクを従来のインクジェット・プリンタで使用する
と、良好な保守特性を示し、代表的な6種類の紙に印
刷して試験した場合、良好な光学密度を示した。

【0077】

【発明の効果】本発明のインクジェット・プリンタ用顔

料インク組成物は、特定の補助溶媒系を含有するため、
安定性、光学密度、粘度、印刷特性(耐水性、耐光性、
印刷ページにおけるフェザリングとインクのランニング
の低減)、プリンタ不使用時のプリンタ・ジェットの目
詰まりの改善、などの点において優れた特性を示す。

フロントページの続き

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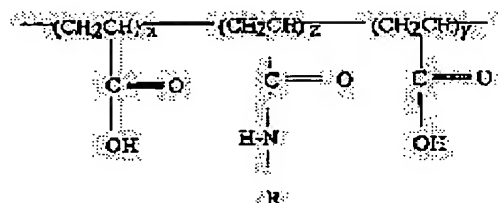
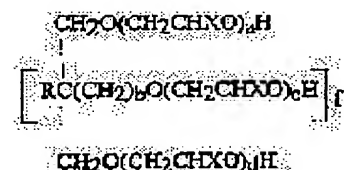
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(54) INK COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain an ink composition for ink jet printers, having satisfactory maintenance properties and excellent optical density and suitability for printing by mixing a pigment with a polymer dispersant therefor, a water-base carrier and a specified auxiliary solvent mixture.

SOLUTION: This composition comprises 1-10wt.% pigment, 0.1-10wt.% polymer dispersant [e.g. a compound represented by formula II (wherein $x+y=20-200$; z is 1-10; and R is a 6-36C alkyl), 50-93wt.% water-based carrier (e.g. a mixture of water with e.g. 1,5-pentanediol) and 5-40wt.% auxiliary solvent mixture. The solvent mixture comprises 1,3-propanediol or 1,4-butanediol (a), a polyethylene glycol having a molecular weight of 200-3,400 or a mixture (b1) thereof with a polypropylene glycol and a compound (b2) represented by formula I [wherein X is H or methyl; R is H, a 1-4C alkyl or the like; (b) is 0 or 1; $a+d+f(c+e)=2-100$; and (f) is 1-6]. The weight ratio $a:(b1+b2)$ is 70:30 to 30:70.



II

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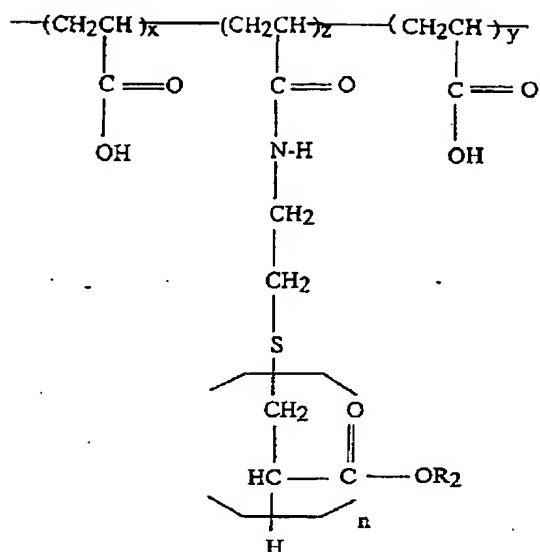
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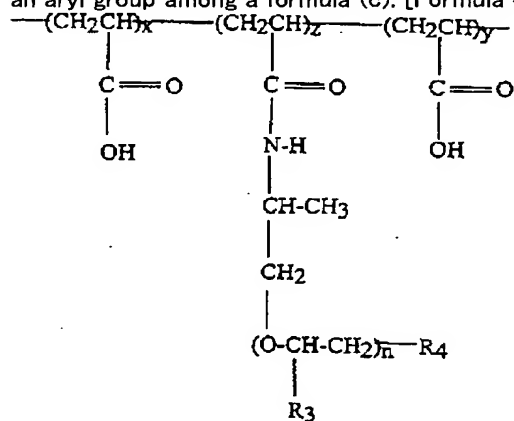
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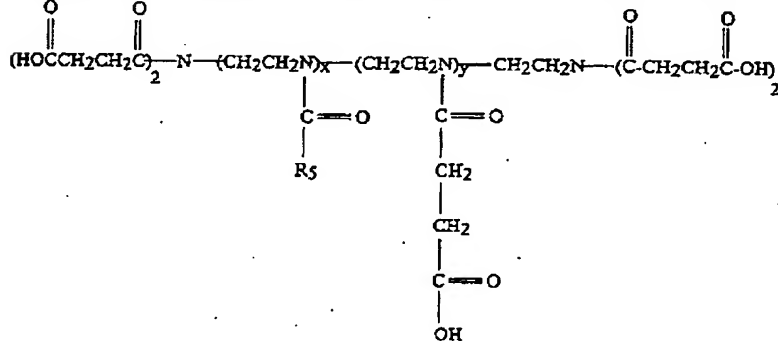
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For $x+y$, about 20 - about 200 z of about 1 - about 10 n are [about 2 - abbreviation 40, and R_2] an alkyl group or an aryl group among a formula (c). [Formula 4]



For about 20 - about 200 z , about 1 - abbreviation 10, and R_3 are [$x+y$ / H, CH₃, or OCH₃ and n of H, or CH₃ and R_4] about 10 - abbreviation 60 among a formula (d). [Formula 5]



y of about 6 - Abbreviation 20 and x is [about 1 - abbreviation 5, and R_5] the alkyl groups of C6-C30 among a formula.

[Claim 8] The aforementioned aqueosity carrier Water; or ethylene glycol, 1 and 2, 6-hexane triol, A thiodiglycol, a hexylene glycol, a diethylene glycol, Pentanediol, hexandiol, a lauric-acid propylene glycol, A glycerol, the ethylene glycol monomethyl (or monoethyl) ether, The diethylene-glycol methyl (or ethyl) ether, the triethylene-glycol monomethyl (or monoethyl) ether, A methanol, ethanol, propanol, a butanol, an acetone, a tetrahydrofuran, A dioxane, ethyl acetate, sulfolanes, N-methyl pyrrolidone, gamma-butyrolactone, The ink constituent according to claim 7 characterized by being mixture [of the organic solvent and water which were chosen from the group which consists of 2-pyrrolidone, a 1-methyl-2-pyrrolidone, 1-(2-hydroxyethyl)-2-pyrrolidones, and such mixture]:

[Claim 9] The ink constituent according to claim 8 characterized by being chosen from the group which the aforementioned pigment becomes from carbon black, a titanium dioxide, an iron oxide, and color pigments.

[Claim 10] The ink constituent according to claim 9 characterized by containing about 0.5 % of the weight - about 4%

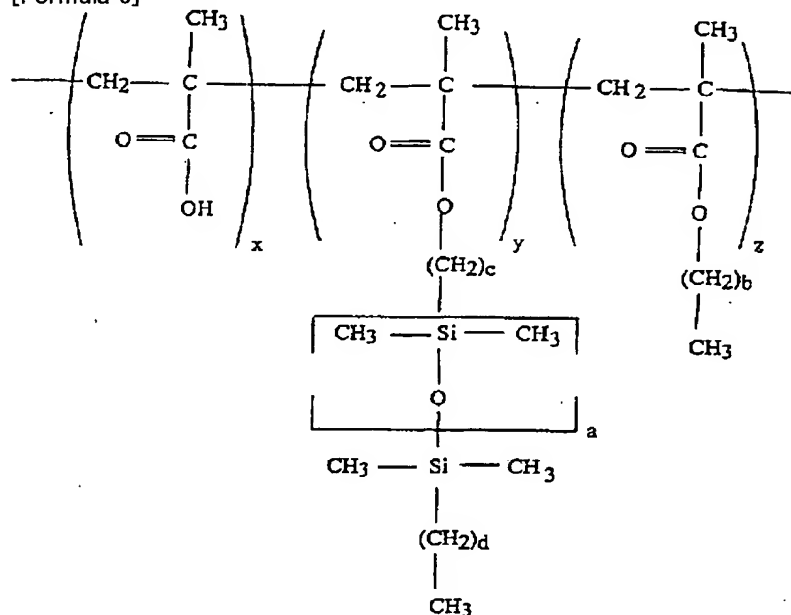
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of the weight of an insoluble pigment.

[Claim 11] The aforementioned polymer dispersant has about 1,500 – about 20,000 molecular weight. (a) It has a hydrophilic polymer segment, and (b) about 400 to about 3,000 molecular weight. The hydrophobic polymer segment which has a stable siloxyl substituent to hydrolysis. It has (c) about 200 to about 2,000 molecular weight in a row. A reactive-surface-active-agent macromolecule object, The ink constituent according to claim 9 characterized by being a protective colloid macromolecule object and a graft copolymer containing the stabilization segment chosen from the group which consists of non-siloxyl hydrophobic monomers.

[Claim 12] The ink constituent according to claim 11 with which the aforementioned polymer dispersant is characterized by having the following formula in a principal chain.

[Formula 6]



the inside of a formula, and x — about 5 – about 100 y — about 1 – about 2 z — about 1 – about 5 a — about 3 – about 45 b — about 3 – about 29 c — about two to 8 d — 0 – it is about 7

[Claim 13] The aforementioned auxiliary solvent mixture is (2) to (1) 1 and 3-propanediol or 1, 4-butanediol, and a row. Ink constituent according to claim 11 characterized by including the matter chosen from the group which consists of following (i) – (iii).

(i) For hydrogen and R, X is [hydrogen and b / 0 and f / 1 and a+d+f (c+e)] what is 26, and such (iii) mixture at the condensation product of the polyethylene glycol and the (ii) aforementioned polyol which have about 200 – about 3,400 molecular weight, and an oxidation alkylene.

[Claim 14] The ink constituent according to claim 13 characterized by containing about 10 % of the weight – about 20% of the weight of the above-mentioned auxiliary solvent mixture.

[Claim 15] The aforementioned auxiliary solvent mixture is (2) to (1) 1, 3-propanediol, and a row. Ink constituent according to claim 14 characterized by including the matter chosen from the group which consists of following (i) – (iii).

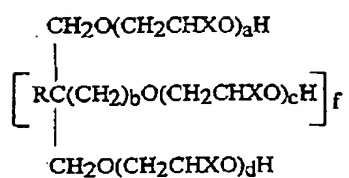
(i) For hydrogen and R, X is [hydrogen and b / 0 and f / 1 and a+d+f (c+e)] what is 26, and such (iii) mixture at the condensation product of the polyethylene glycol and the (ii) aforementioned polyol which have about 400 molecular weight, and an oxidation alkylene.

[Claim 16] The ink constituent according to claim 15 characterized by above (1) and weight ratio [of (2)] (1): (2) being about 50:50.

[Claim 17] The ink constituent according to claim 16 which is mixture [of the organic solvent and water which were chosen from the group which the aforementioned aqueous carrier becomes from water, or 1,5-pentanediol, 1, 6-hexandiol, 1, 7-heptane diol, n-propanol, and such mixture];, and is characterized by including 50 % of the weight of ****, about 50 % of the weight of organic solvents –, and about 0.1 % of the weight of 99.9 % of the weight of **** and organic solvents.

[Claim 18] (1) the matter chosen as 1 and 3-propanediol or 1, 4-butanediol, and a row from (i) of (2) following – (iii) a group — containing — ** (1) and weight ratio [of (2)] (1): (2) — about 70:30– the auxiliary solvent mixture which is about 30:70 (i) Condensation product of the polyethylene glycols which have about 200 – about 3,400 molecular weight, the polyol which has the mixture of polyethylene glycols and polypropylene glycols, and the formula of (ii) following in a row, and an oxidation alkylene, [Formula 7]

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the inside of a formula, and X — H, or CH₃ and R — the alkyl group of H, C₁–C₄, or CH₂O (CH₂CH₂O) — eH, b₀ or 1, and a+d+f (c+e) — about 2 – about 100 f — about 1– such (iii) mixture which is about 6

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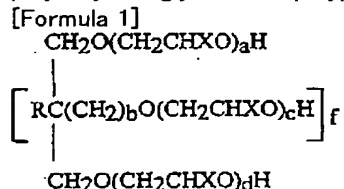
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CLAIMS

[Claim(s)]

(a) about 1 % of the weight - about 10% of the weight of a pigment, and (b) - about 0.1 % of the weight - about 10% of the weight of the polymer dispersant for the above-mentioned pigments - (c) It is (d) to about 50 % of the weight - about 93% of the weight of a water carrier, and a row. (1) 1 and 3-propanediol or 1, 4-butanediol, And the matter chosen from (i) of (2) following - (iii) a group is included. The water-color-ink constituent containing about 5 % of the weight - about 40% of the weight of the auxiliary solvent mixture whose ** (1) and weight ratio [of (2)] (1): (2) is about 70:30 - abbreviation 30:70 suitable for use of an ink jet printer. (i) Condensation product of the polyethylene glycols which have about 200 - about 3,400 molecular weight, the polyol which has the mixture of polyethylene glycols and polypropylene glycols, and the formula of (ii) following in a row, and an oxidization alkylene,



the inside of a formula, and X - H, or CH₃ and R - the alkyl group of H, C₁-C₄, or CH₂O (CH₂CH₂O) - eH, b₀ or 1, and a+d+f (c+e) - about 2 - about 100 f - about 1- such (iii) mixture which is about 6

[Claim 2] The ink constituent according to claim 1 characterized by the aforementioned auxiliary solvent mixture containing the matter chosen as (1) 1 and 3-propanediol or 1, 4-butanediol, and a row from (i) of (2) following - (iii) a group.

(i) Those 1 and whose a+d+f (c+e) it is the condensation product of the polyethylene glycol and the (ii) above-mentioned polyol which have about 200 - about 3,400 molecular weight, and an oxidization alkylene, and 0 and f are [the inside of a formula, and X / hydrogen and R] 26 for hydrogen and b, such (iii) mixture.

[Claim 3] The ink constituent according to claim 2 characterized by containing about 10 % of the weight - about 20% of the weight of the aforementioned auxiliary solvent mixture.

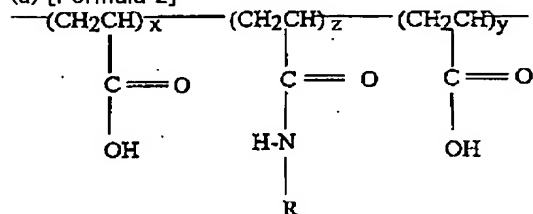
[Claim 4] The ink constituent according to claim 3 characterized by a polyethylene-glycol component (i) being the polyethylene glycol which has about 400 molecular weight in the aforementioned auxiliary solvent mixture.

[Claim 5] The ink constituent according to claim 4 characterized by the aforementioned auxiliary solvent mixture being the mixture of 1 and 3-propanediol and the polyethylene glycol which has about 400 molecular weight.

[Claim 6] The ink constituent according to claim 4 characterized by above (1) and weight ratio [of (2)] (1): (2) being about 50:50.

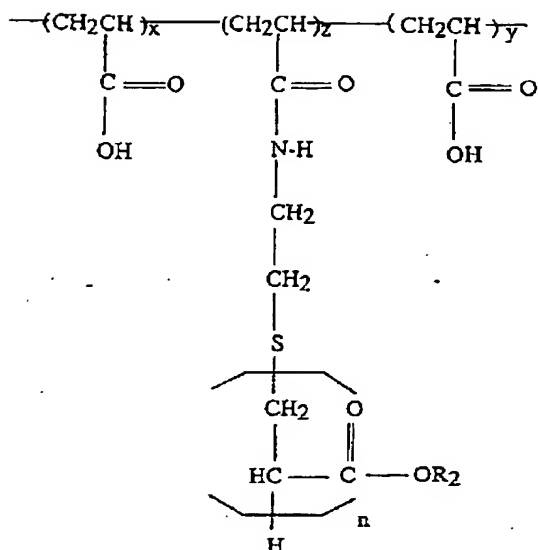
[Claim 7] The ink constituent according to claim 1 characterized by including the structural unit chosen from the group which the aforementioned polymer dispersant becomes from following (a) - (d) in a principal chain.

(a) [Formula 2]

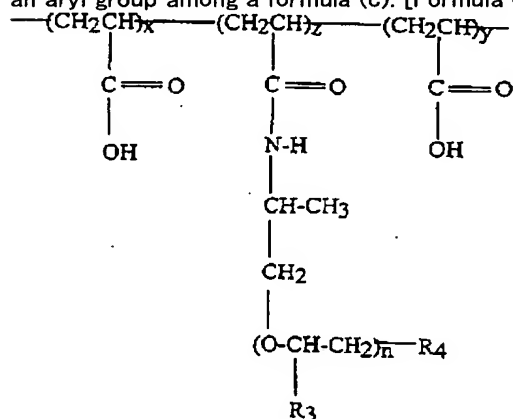


For x+y, the alkyl group of C₆-C₃₆, or R₁ and R₁ are [about 20 - about 200 z of about 1 - abbreviation 10 and R] the alkyl group of C₄-C₂₀ among a formula (b). [Formula 3]

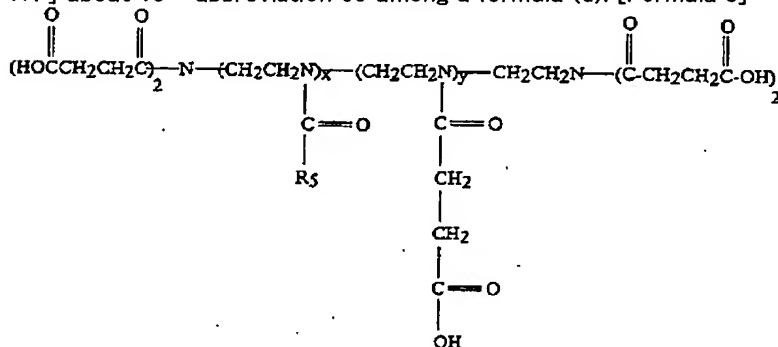
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For x+y, about 20 - about 200 z of about 1 - about 10 n are [about 2 - abbreviation 40, and R2] an alkyl group or an aryl group among a formula (c). [Formula 4]



For about 20 - about 200 z, about 1 - abbreviation 10, and R3 are [x+y / H, CH3, or OCH3 and n of H, or CH3 and R4] about 10 - abbreviation 60 among a formula (d). [Formula 5]



y of about 6 - Abbreviation 20 and x is [about 1 - abbreviation 5, and R5] the alkyl groups of C6-C30 among a formula.

[Claim 8] The aforementioned water carrier Water; or ethylene glycol, 1 and 2, 6-hexane triol, A thiodiglycol, a hexylene glycol, a diethylene glycol, Pentanediol, hexandiol, a lauric-acid propylene glycol, A glycerol, the ethylene glycol monomethyl (or monoethyl) ether, The diethylene-glycol methyl (or ethyl) ether, the triethylene-glycol monomethyl (or monoethyl) ether, A methanol, ethanol, propanol, a butanol, an acetone, a tetrahydrofuran, A dioxane, ethyl acetate, sulfolanes, N-methyl pyrrolidone, gamma-butyrolactone, The ink constituent according to claim 7 characterized by being mixture [of the organic solvent and water which were chosen from the group which consists of 2-pyrrolidone, a 1-methyl-2-pyrrolidone, 1-(2-hydroxyethyl)-2-pyrrolidones, and such mixture]:

[Claim 9] The ink constituent according to claim 8 characterized by being chosen from the group which the aforementioned pigment becomes from carbon black, a titanium dioxide, an iron oxide, and color pigments.

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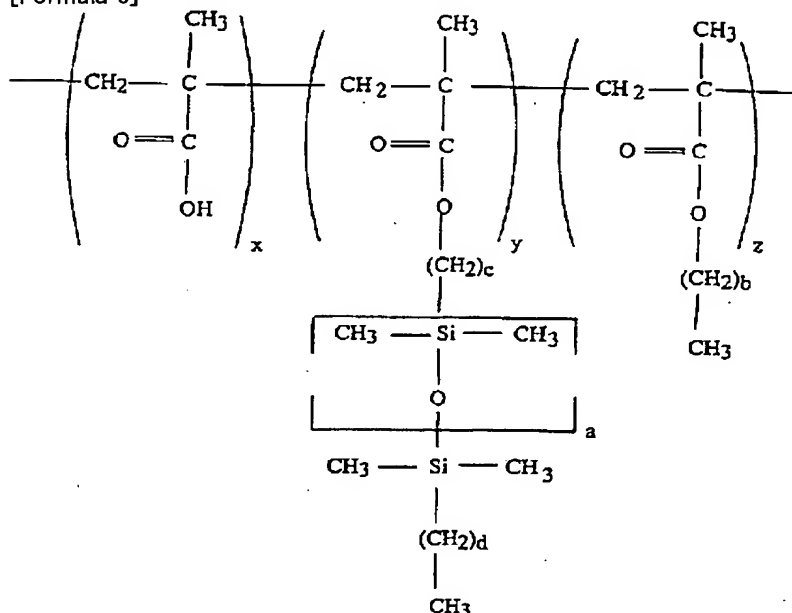
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of the weight of an insoluble pigment.

[Claim 11] The aforementioned polymer dispersant has about 1,500 – about 20,000 molecular weight. (a) It has a hydrophilic polymer segment, and (b) about 400 to about 3,000 molecular weight. The hydrophobic polymer segment which has a stable siloxyl substituent to hydrolysis, It has (c) about 200 to about 2,000 molecular weight in a row. A reactive-surface-active-agent macromolecule object, The ink constituent according to claim 9 characterized by being a protective colloid macromolecule object and a graft copolymer containing the stabilization segment chosen from the group which consists of non-siloxyl hydrophobic monomers.

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[Formula 6]



the inside of a formula, and x — about 5 — about 100 y — about 1 — about 2 z — about 1 — about 5 a — about 3 — about 45 b — about 3 — about 29 c — about two to 8 d — 0 — it is about 7

[Claim 13] The aforementioned auxiliary solvent mixture is (2) to (1) 1 and 3-propanediol or 1, 4-butanediol, and a row. Ink constituent according to claim 11 characterized by including the matter chosen from the group which consists of following (i) – (iii).

(i) For hydrogen and R, X is [hydrogen and b / 0 and f / 1 and a+d+f (c+e)] what is 26, and such (iii) mixture at the condensation product of the polyethylene glycol and the (ii) aforementioned polyol which have about 200 – about 3,400 molecular weight, and an oxidation alkylene.

[Claim 14] The ink constituent according to claim 13 characterized by containing about 10 % of the weight – about 20% of the weight of the above-mentioned auxiliary solvent mixture.

[Claim 15] The aforementioned auxiliary solvent mixture is (2) to (1) 1, 3-propanediol, and a row. Ink constituent according to claim 14 characterized by including the matter chosen from the group which consists of following (i) – (iii).

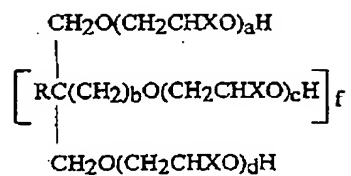
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[Claim 16] The ink constituent according to claim 15 characterized by above (1) and weight ratio [of (2)] (1): (2) being about 50:50.

[Claim 17] The ink constituent according to claim 16 which is mixture [of the organic solvent and water which were chosen from the group which the aforementioned aqueous carrier becomes from water; or 1,5-pentanediol, 1, 6-hexandiol, 1, 7-heptane diol, n-propanol, and such mixture], and is characterized by including 50 % of the weight of ****, about 50 % of the weight of organic solvents –, and about 0.1 % of the weight of 99.9 % of the weight of **** and organic solvents.

[Claim 18] (1) the matter chosen as 1 and 3-propanediol or 1, 4-butanediol, and a row from (i) of (2) following – (iii) a group — containing — ** (1) and weight ratio [of (2)] (1): (2) — about 70:30— the auxiliary solvent mixture which is about 30:70 (i) Condensation product of the polyethylene glycols which have about 200 – about 3,400 molecular weight, the polyol which has the mixture of polyethylene glycols and polypropylene glycols, and the formula of (ii) following in a row, and an oxidation alkylene, [Formula 7]

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the inside of a formula, and X — H, or CH₃ and R — the alkyl group of H, C₁–C₄, or CH₂O (CH₂CH₂O) — eH, b0 or 1, and a+d+f (c+e) — about 2 – about 100 f — about 1– such (iii) mixture which is about 6

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the ink constituent used for an ink jet printer.

[0002]

[Description of the Prior Art] Ink-jet printing is performed by injecting ink from a nozzle to paper or other print media. Ink can be made to inject by various kinds of methods towards a medium. For example, in electrostatic printing, ink is injected by the electrostatic field towards a medium from a nozzle. In the procedure of other ink-jet printings known as a squeeze tube, the piezoelectric device is used into an ink nozzle. Ink is transported to print media through a nozzle by the electric distortion of a piezoelectric device. In the procedure of other ink-jet printings in which thermal ** is known as bubble ink-jet printing, when the bubble of a gaseous phase expands within a nozzle, ink is injected towards print media from a nozzle. The print processes of these various kinds are indicated by issue (refer to Chapter 13 "ink-jet printing (Ink Jet Printing)" especially) in DABEKKU (Durbeck) and edited by Shache (Sherr) "hard copy output unit (Output Hard Copy Devices)", and Academic Press (Academic Press) 1988.

[0003] The ink constituent used for an ink jet printer usually contains the organic solvent of deionized water, water solubility, or water and compatibility, and a coloring agent. Generally, a coloring agent is the color of fusibility. A low and chemicals-proof nature have [the thermal stability whose printing quality is not good] many problems of a low, being easy to oxidize in the ink [it is regrettable and] which contains a fusibility color especially including bleeding, feathering, etc. of ink which plugging produces in an injection channel by the evaporation of a solvent which is not [a low and lightfastness] good, or change of the solubility of a color and which a color crystallizes.

[0004] Many of these problems are solvable by using an insoluble pigment instead of the fusibility color used for ink prescription. Generally, the pigment is excellent in the property as compared with the color, and excellent in respect of the ability to also suit especially water resistance, lightfastness, thermal stability, oxidation stability, and the paper coated or processed also at a regular paper. However, in order not to dissolve in an ink constituent, therefore to make it distribute, some new problems produce a pigment. The stability of ink is very important for maintaining the homogeneity of a property, and a row in the point of making it both not get a pigment blocked in an ink jet, while not using it. It is ideal to make the amount of a pigment required in an ink constituent, of course into the minimum from the reason of both stability and cost. However, if the amount of the pigment in an ink constituent is reduced, the optical density of a picture will fall. Furthermore, in order to secure required stability, while the balance of composition is required, therefore has suitable viscosity in an ink jet printer using a constituent, when it prints on paper, it is important [water resistance and lightfastness are good, and] that running and feathering are also the minimum. It was very difficult to develop ink prescription which optimized all of these properties until now. Adjusting the dispersant and solvent system of an ink constituent for the purpose of maintaining and optimizing the balance of these properties that conflict in many cases as common practice was performed. However, prescription which optimized all these properties, without using a specific polymer dispersant before this invention was not attained.

[0005] The ink constituent for ink jets which contains the auxiliary solvent of a water carrier medium, pigment dispersion liquid, and a polyol and an oxidization alkylene in the U.S. Pat. No. 5,180,425 specification of the matric (Matrick) on January 19, 1993 is indicated. The life of ink jet printer ability is lengthened and these ink is taught that there is coat-proof formation nature. RAIPO nick (Liponic) EG-1 is one of the indicated desirable auxiliary solvents. The polyethylene glycol is contained in other solvents used for this patent.

[0006] Pigment dispersion liquid, the aquosity carrier medium, and a polyol, the condensation product of an oxidization alkylene and the ink constituent containing the auxiliary solvent mixture containing a cyclic-amide derivative for ink jets are indicated by the U.S. Pat. No. 5,302,197 specification of wick Lamaism NAIKE (Wickramanayke) on April 12, 1994. It is taught that RAIPO nick EG-1 is useful as a condensation-product component of a polyol and an oxidization alkylene.

[0007] A water carrier medium, a specific alkyl polyol ether auxiliary solvent, and the ink for ink jets that consists of pigment dispersion liquid (what stabilized the pigment particle with the dispersant) are indicated by the Europe patent No. 603,469 application of Chillan and others on June 29, 1994 (Chan). It is taught that these ink has viscosity, surface tension, plugging prevention of a nozzle, printing quality, light stability, bleeding-proof nature, and waterproof good balance. 1, 2, and 3-butane triol is contained in the solvent used by invention of an indication.

[0008] A clear image is formed in the U.S. Pat. No. 4,597,794 specification of OTA and others on July 1, 1986, and ink prescription used for the ink-jet printing process said to have a good physical property is indicated. A

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polyethylene glycol and 1, 2, and 6-hexane triol are contained in the solvent indicated especially in order to use it for this ink.

[0009] Giving characteristic mixture, when optimizing a property was found out by using the specific auxiliary solvent mixture which contains 1 and 3-propanediol or 1, and 4-butanediol with either the polyethylene glycol of (a) low molecular weight, a related compound or the condensation product of the (b) polyol and an oxidization alkylene for the water-color-ink constituent containing the dispersion liquid of an insoluble pigment. That is, the property these constituents excelled [property] in stability, optical density, viscosity, the printing property (running of feathering in water resistance, lightfastness, and the printed page and ink is the minimum), and the row in points, such as a problem (the blinding of the printer jet at the time of printer un-using it is the minimum) of printer maintenance, (even when low pigment concentration is used) is acquired. About the combination of the specific auxiliary solvent shown by this invention, neither a publication nor suggestion has each in the above-mentioned patent.

[0010]

[Problem(s) to be Solved by the Invention] Therefore, the purpose of this invention is to offer the pigment ink constituent with which it has been improved for [containing a specific auxiliary solvent system] ink jet printers.

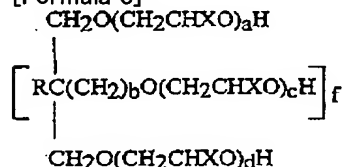
[0011]

[Means for Solving the Problem] Other purposes and features of this invention become clear by the following indication.

[0012] In the 1st mode of this invention, the pigment of 1 % of the weight - about 10 % of the weight of (a) abbreviation, (b) About 0.1 % of the weight - about 10% of the weight of the polymer dispersant for the above-mentioned pigments, the aqueosity carrier of 50 % of the weight - about 93 % of the weight of (c) abbreviation, and (d) (1) 1 and 3-propanediol or 1, and 4-butanediol, (2) The water-color-ink constituent containing about 5% - about 40% of auxiliary solvent mixture containing the matter chosen from the following (i) - (iii) a group suitable for use of an ink jet printer is offered. (i) Condensation product of the polyethylene glycols which have about 200 - about 3,400 molecular weight, the polyol which has the mixture of polyethylene glycols and polypropylene glycols, and the formula of (ii) following in a row, and a polyacid-ized alkylene.

[0013]

[Formula 8]



[0014] the inside of a formula, and X -- H, or CH₃ and R -- the alkyl group of H, C₁-C₄, or CH₂O (CH₂CH₂O) -- eH, b₀ or 1, and a+d+f (c+e) -- about 2 - about 100 f -- about 1- it is about 6 (iii) Such mixture. In addition, above-mentioned (1) ratio [of : (2) / weight] (1): (2) is about 70:30 - abbreviation 30:70.

[0015] The 2nd mode of this invention is related with the auxiliary solvent mixture shown above (d).

[0016] The percentage and the ratios which were used for this specification are "weight %" and a "weight ratio", unless it otherwise specifies. The molecular weight used for this specification is number average molecular weight, unless it otherwise specifies.

[0017]

[Embodiments of the Invention] this invention relates to the water-color-ink constituent suitable for using it for an ink jet printer. These constituents contain the polymer dispersant (a pigment and a dispersant exist in the constituent as dispersion liquid), the aqueosity carrier, and the specific auxiliary solvent mixture for an insoluble pigment and a pigment. Each of these required components is explained in detail below with some additional components.

[0018] a polymer dispersant -- the constituent of this invention -- setting -- about 0.1% - about 10% of the last component -- it is contained about 0.5% to about 4% most preferably about 0.25% to about 5% both the anion nature by which it is known for the industry that it is suitable for using it for the polymer dispersant suitable for using it by this invention as a dispersant of the ink manufacture object for ink jets cation nature and a non-ionicity polymer -- although -- it is contained The example of such a material is indicated by the U.S. Pat. No. 5,310,778 specification of Shore and others on May 10, 1994 appended to this specification as reference (Shor). A homopolymer, a copolymer, the letter polymer of branching, or a graft polymer is sufficient as such a polymer dispersant. Moreover, a random polymer or a block polymer is sufficient.

[0019] The block copolymer of AB, BAB, and ABC is one sort of a polymer dispersant useful to this invention. Desirable things are AB and BAB which were guided from at least one sort of alkyl acrylics or a methacrylic ester and an amine substitution acrylic, or the monomers of a methacrylic ester, and an ABC block copolymer. MA [on February 4, 1992 when desirable AB and BAB block copolymers, and these processes were appended to this specification as reference] -- it is indicated by the U.S. Pat. No. 5,085,698 specification of Ma) and others

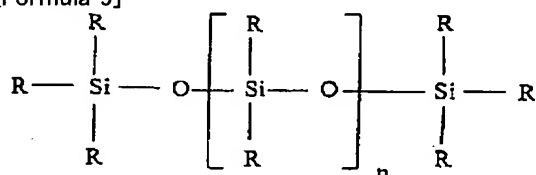
[0020] A polymer dispersant useful to operation of this invention usually tends to combine a hydrophobic segment with the pigment particle in an ink constituent including both polymer segments of a hydrophobic property and a hydrophilic property, it is tended by the liquid ink medium to carry out the solvation of the hydrophilic segment, and it stabilizes dispersion liquid according to these, a three-dimensional mechanism, and/or an ionicity mechanism.

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[0021] The desirable polymer dispersant of a kind used by this invention contains the block or graft copolymer containing a hydrophilic polymer segment and the hydrophobic polymer segment which contains a stable siloxyl substituent to hydrolysis. Especially a desirable thing is a graft copolymer containing a hydrophilic polymer segment (especially acrylate or a methacrylate copolymer) and the hydrophobic polymer segment guided from the macromolecule object which has the following formula among the groups of these dispersants.

[0022]

[Formula 9]



[0023] n is the low-grade alkyl (C1-C6) or siloxyl which 2-16R became independent of, respectively among a formula. Such material is indicated by the U.S. patent application 08th/No. 360,199 specification of December 21, 1994 and beaches (Beach) appended to this specification as reference.

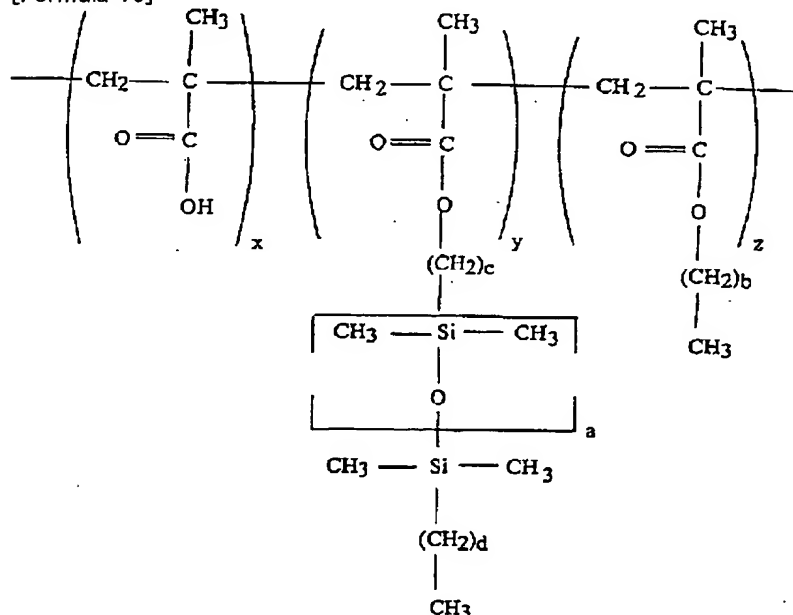
[0024] The desirable polymerization nature powder of other kinds is a graft copolymer containing the hydrophobic polymer segment which has about 1,500 - about 20,000 molecular weight, has a stable siloxyl substituent to (a) hydrophilic-property polymer segment and (b) hydrolysis, and has about 400 - about 3,000 molecular weight, and the stabilization segment chosen from the group which becomes a row from the surface activity macromolecule object of (c) reactivity, a protective colloid macromolecule object, and a non-siloxyl hydrophobic monomer.

[0025] Desirable monomer ratio (a) : (b) is about 10:1 - abbreviation 100:1, and desirable monomer ratio (b): (c) is about 1:0.5 - abbreviation 1:5. A desirable hydrophilic polymer segment has a bitter taste relay torr or the most desirable meta-chestnut rhe torr polymer matter including a carboxy substituent. A desirable siloxane content hydrophobic polymer segment is the poly dialkyl siloxane macromolecule object which has an acryloyl or a methacryloyl machine at the end. The most desirable hydrophobic segment is ** which has about 400 - about 2,000 molecular weight, and has a dimethyl polysiloxyl machine. A desirable stabilization segment Stearylacrylate, stearyl methacrylate, Laurylacrylate, lauryl methacrylate, nonyl-phenol acrylate, Nonyl-phenol methacrylate, n - about 1-nonyl phenoxy poly (ethyleneoxy) n methacrylate which is about 40; n - about 1-nonyl phenoxy poly (ethyleneoxy) n acrylate which is about 40; n - about 5-methoxy poly (ethyleneoxy) n methacrylate which is about 40; Methoxy poly whose n is about 5 - abbreviation 40 (Ethyleneoxy) n acrylate; Stearyl oxy-poly whose n is about 1 - abbreviation 20 (Ethyleneoxy) n methacrylate; Stearyl oxy-poly whose n is about 1 - abbreviation 20 (Ethyleneoxy) n acrylate; - fluoridation C1-C18 alkyl methacrylate; - fluoridation C1-C18 alkyl acrylate; - poly (propylene glycol) methyl-ether methacrylate; - poly (propylene glycol) methyl-ether acrylate - Poly (Propylene glycol) 4-nonylphenyl ether methacrylate; - poly (propylene glycol) 4-nonylphenyl ether acrylate; - polyethylene-oxide; which has a metacryloxy machine and a trimethylsiloxyl machine at the end - Polyethylene-oxide; which has an acrylic oxy-basis and a trimethylsiloxyl machine, and such mixture are included in an end.

[0026] The most desirable thing has the following formula in a principal chain with this kind of polymer dispersant.

[0027]

[Formula 10]



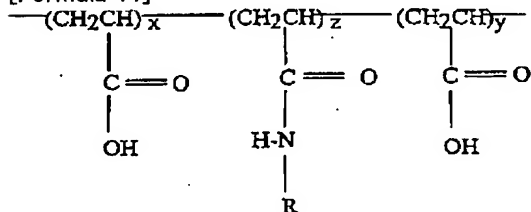
[0028] The inside of a formula, 3; x - about 5- about 100 - desirable - about 15 - about 50 y - about 1- about

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2 — desirable — about 1 z — about 1 — about 5 — desirable — about 1 — a — about 3 — about 45 — desirable — about 9 b — about 3 — about 29 — desirable — about 15 — about 17 c — about 2 — about 8 — desirable — about — d — 0 — about 7 — it is about 3 preferably In addition, it is within the limits of this invention which all the structural units expressed with x, and y and z are distributing at random in the principal chain of a polymer. These polymer dispersants are indicated by the U.S. patent application "the polymer dispersant for pigment use ink" of ***** of the beaches (Beach) appended to this specification as reference. The end group of the dispersant of this invention is not limited. For the purpose of explanation, it is contained like [a thio substitution hydrocarbon] hydrogen. [0029] The polymer dispersant of other kinds is indicated by the U.S. patent application 08th/No. 360,200 specification of December 21, 1994 and beaches (Beach) appended to this specification as reference. These matter is the graft polymers containing the hydrophobic segment side chain which has one side chain combined with one principal chain as preferably as the principal chain of the hydrophilic polyacrylic acid of the weight average molecular weight of about 1,000 — about 5,000 between. This kind of desirable polymer has one of the following structure expressions in a principal chain.

[0030]

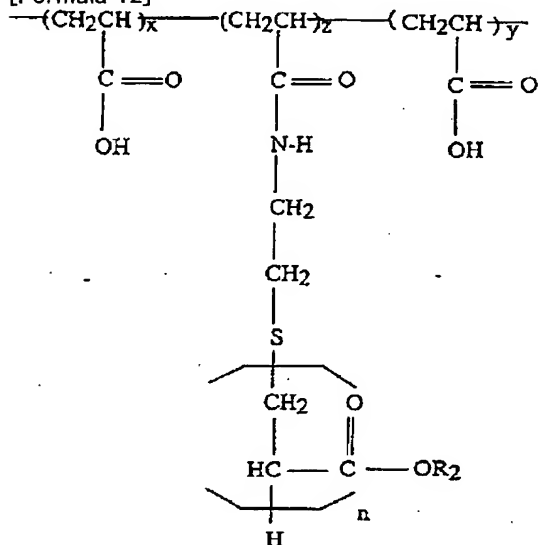
[Formula 11]



[0031] x+y is [about 1 — abbreviation 10, and R of about 20 — about 200 z] the alkyl group of C6-C36, or the following R1 among a formula. R1 is the alkyl group or the following basis of C4-C20.

[0032]

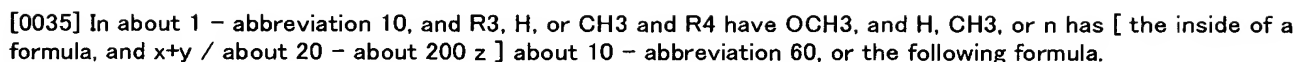
[Formula 12]



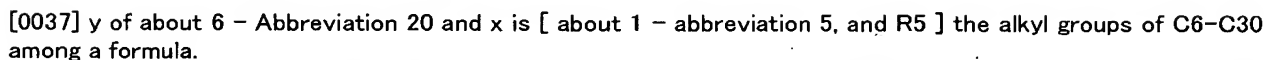
[0033] the inside of a formula, and x+y — about 20 — about 200 z — about 1 — about 10 n — about 2 — about 40 and R2 — an alkyl group or an aryl group — desirable — a butyl — or [0034]

[Formula 13]

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[Formula 14]



[0038] The graft copolymer dispersant of this invention is low molecular weight comparatively, in order to acquire the stability of a particle, and in order to use it for the stable ink for ink-jet printing, the low need has viscosity. For this reason, the polar-solvent polymerization method for generating a copolymer is chosen. The molecular weight of a copolymer and homogeneity are controlled by such method by maintaining the solubility of not only the copolymer obtained but all start raw materials (it is a chain transfer agent to a free radical initiator, a hydrophobic property and a hydrophilic monomer, and a row). In order to write a prescription to ink-jet printing and to make an aqueous medium suspend the compounded copolymer, it needs to collect copolymers from the polar organic solvent in reaction mixture, and it is necessary to make it dissolve them in water. The copolymer recovery method from a typical polar polymerization solvent includes the following processes.

1. The solution of a copolymer is added to non-solvents, such as a hexane, a polymer is settled from a solution, this refines a copolymer, vacuum filtration of the 2. precipitate is carried out, and 3. copolymer precipitate is dried.

[0039] Next, copolymer powder can be dissolved in an aqueous base and it can be used for generation of the ink for ink-jet printing. This method has high cost and is superfluously complicated. [of cost]

[0040] The desirable method for collecting the dispersants of a copolymer from a polar organic polymerization solvent improves printing quality which decreases it not only merely collects the dispersants of a copolymer, but that the ink-jet ink generated from these dispersants forms a satellite and a splatter. Specifically, these desirable methods include the following process.

1. Dissolve in an aqueous base and exchange 2. solvent, after evaporating a solvent.

[0041] At solvent evaporation and a dissolution process, vacuum tray dryness, rotation evaporation dryness, drum dryness, a turning-circle cylinder vacuum drying, or spray drying evaporates a polar solvent from a copolymer first by the standard method of changing the solution of a copolymer into dryness powder. Next, the dry copolymer powder is dissolved in an aqueous base, and it enables it to use it for generation of the ink of the pigment for ink jets.

[0042] a solvent exchange-buffering-method process — about 35% — about 60% of the polar solvent in a polymerization reactor (preferably about 50%) — distillation — removing — deionized water and an aqueous base (for example, KOH solution) — adding — pH — about 4.5– about 6.5 — it adjusts to about 5 preferably In order for the boiling point to make a solvent distill from water until all polar solvents amount to about 100 degrees C from which temperature is removed in the case of a low polar solvent, the temperature of this mixture is raised slowly. (This process cannot be used when the boiling point of a polar solvent is higher than the boiling point of water.) further — an aqueous base (for example, KOH solution) — this solution — in addition, pH — about 7– about 8.5 —

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about 7.5 is raised preferably Subsequently, this solution is used for prescription of the pigment ink for ink jets. [0043] The 2nd component of the ink constituent of this invention is a pigment which is an insoluble coloring agent. the constituent of this invention — a pigment — the last constituent — receiving — about 0.1% — about 10% — about 0.5% — 4% exists most preferably about 0.25% to about 5% Actually, one of the important advantages of this invention enables prescription of ink which has low pigment concentration (for example, 0.5 — 4%), and moreover, it is quality and is offering the outstanding optical density. February 4, 1992 and MA (appended to this specification as reference as a pigment useful to operation of this invention — all of the well-known conventional pigment can be used in this industry that is indicated by the U.S. Pat. No. 5,085,698 specification of Ma) and others Even if it uses it independently, you may use a pigment, combining.

[0044] The particle of a pigment needs to have [an ink-jet printer, especially a diameter] small ink enough so that the inside of the injection nozzle which is usually about 10 micrometers — about 50 micrometers can be flowed freely. Particle size affects the distributed stability of an important pigment through the life of ink again. The Brownian motion of a particle is useful to condensation prevention of a particle, and, thereby, a product is stabilized further. A useful size range is about 0.05 micrometers — about 15 micrometers. The range of the particle size of a pigment is about 0.05 micrometers — about 5 micrometers, and the range of it is about 0.05 micrometers — about 1 micrometer most preferably. A pigment can be used also with the form which carried out [the dry form or] humidity. For example, a pigment is usually manufactured in a water medium and is obtained as a filter press cake containing water. With the form of this filter press cake, a pigment is not condensed like [in the case of a dryness form]. Therefore, the pigment of the form of the filter press cake containing water does not need to perform solution condensation in the manufacturing process of ink like [at the time of using the dry pigment].

[0045] The particle of a metal or a metallic oxide can also be used for operation of this invention. For example, the metal and the metallic oxide are suitable for manufacture of the ink for magnetic ink jets. The oxide of a particle, for example, a silica, an alumina, a titania, etc. can be used. Furthermore, the pulverized metal particles, for example, copper, iron, steel, aluminum, and alloys can be chosen because of a suitable use.

[0046] there are inorganic pigments, such as organic pigment; titanium oxide, such as color lake; nitroglycerine pigments, such as polycyclic formula pigment; basic dye lakes, such as azo pigment; phthalocyanine pigments, such as an azo lake, a disazo condensation pigment, and a chelate azo pigment, a perylene pigment, an anthraquinone pigment, a Quinacridone pigment, a dioxazine pigment, a thio indigo pigment, an isoindolinone pigment, and a kino FUTARON pigment, and an acid-dye lake, an oximido pigment, an aniline black, and a daylight fluorescent pigment, an iron oxide, and carbon black, etc. in the example A desirable pigment contains titanium oxide, an iron oxide, and carbon black in using it in this invention. For the example of the available pigment of marketing which can be used in this invention Brand name Heliogen Blue L 6901F (BASF), Brand name Heliogen Blue NBD 7010 (BASF), Brand name Heliogen Blue K 7090 (BASF), Brand name Heucophthal Blue GXBT-583D (HYU back), Brand name Irgalite Rubin 4BL (Ciba-Geigy), Brand name Quindo A Magenta (Mobey), brand name Indofast Brilliant scarlet (Mobey), Brand name Hostaperm Scarlett GO (Hoechst), Permanent Rubin F6B (Hoechst), brand name Monastral Scarlett (Ciba-Geigy), Brand name Raven 1170 (COL KEMU), SUPESSHARU black 4A (Degussa AG), Black FW18 (Degussa AG), brand name Sterling NS Black (Cabot), Brand name Sterling NSX 76 (Cabot) Monarch 880 (Cabot), Brand name Tipure R-101 (E. I. du Pont de Nemours), MOGARU L (Cabot), BK 8200 (pole URITCHI) Brand name Heliogen Green K 8683 (BASF), Brand name Heliogen Green L9140 (BASF), Brand name Monastral Red B (Ciba-Geigy), brand name Monastral Violet R (Ciba-Geigy) Brand name Hostaperm Orange GR (Hoechst), brand name Paliogen Orange (BASF), L75-2377 Yellow (Sun KEMU) and L74-1357 Yellow (Sun KEMU), Brand name Hostaperm Yellow H4G (Hoechst), brand name Argazin Yellow 5GT (Ciba-Geigy), Permanent Yellow G3 R-01 (Hoechst), brand-name Novoperm yellow FGL (Hoechst), Brand name Chromophthal Yellow 3G (Ciba-Geigy), HANZA Yellow X (Hoechst), brand name Dalamar Yellow YT-858-D (HYU back), HANZA Brilliant Yellow There is 5GX-02 (Hoechst) etc.

[0047] The 3rd component of the ink constituent of this invention is an aqueous carrier medium. This component is the mixture of water (preferably deionized water) or water, and at least one kind of water-soluble organic solvent. an aqueous carrier component — constituent [of this invention / about 50% of] — about 70% — about 80% exists preferably about 93% Selection of suitable mixture is dependent on the kind of paper in which ink is printed by the drying time required for the requirements for the specific ink prescribed, for example, desirable surface tension, viscosity, the pigment to be used, and pigment ink, and the row etc. As an example of representation of the water-soluble organic solvent which can be chosen (1) Methyl alcohol, ethyl alcohol, n-propyl alcohol, Isopropyl alcohol, n-butyl alcohol, sec-butyl alcohol, t-butyl alcohol, isobutyl alcohol, furfuryl alcohol, Alcohols; (2) acetones, such as a tetrahydrofurfuryl alcohol, Ketones or keto-alcohols; (3) tetrahydrofurans, such as a methyl ethyl ketone and diacetone alcohol, Ether; (4) ethyl acetate, such as a dioxane, an ethyl lactate, an ethylene carbonate, Ester; (5) ethylene glycol, such as a propylene carbonate, a diethylene glycol, A glycerol, the 2-methyl -2, 4-pentanediol, 1 and 2, 6-hexane triol, Polyhydric alcohol, such as a thiodiglycol; (6) ethylene-glycol monomethyl (or monoethyl) ether, The diethylene-glycol monomethyl (or monoethyl) ether, the propylene-glycol monomethyl (or monoethyl) ether, The low-grade alkyl monochrome guided from alkylene glycol, such as the triethylene-glycol monomethyl (or monoethyl) ether and the diethylene-glycol dimethyl (or diethyl) ether, or a diethers; (7) pyrrolidone, a N-methyl-2-pyrrolidone, There are sulfur content compounds, such as nitrogen content cyclic compounds, such as 1 and 3-dimethyl-2-imidazolidinone, (8) dimethyl sulfoxide, and a tetramethylen sulfone. There are lactone and lactams in other useful solvents.

[0048] When using the mixture of water and an organic solvent as a carrier medium by this invention, a medium usually contains 25% of ****, about 75% of organic solvents —, and about 0.1% of 99.9% of **** and organic solvents.

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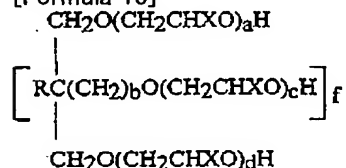
Desirable ratios are 50% of ****, about 50% of organic solvents -, and about 0.1% of 99.9% of **** and organic solvents. Such percentage receives the total weight of an aqueosity carrier medium. What is used for an aqueosity carrier medium in the term of the "organic solvent" used on these specifications should understand that it is not what means that a specific material used as a component of the auxiliary solvent of this invention is included.

[0049] In the desirable organic solvent used for the aqueosity carrier medium component of this invention Ethylene glycol, 1 and 2, 6-hexane triol, a thiodiglycol, Polyhydric alcohol, such as a hexylene glycol and a diethylene glycol; Pentanediol, Glycol ethers, such as diols; lauric-acid propylene glycols, such as hexandiol and homologous-series diols; Glycerol; and the ethylene glycol monomethyl (or monoethyl) ether, The diethylene-glycol methyl (or ethyl) ether, the triethylene-glycol monomethyl (or monoethyl) ether, The low-grade alkyl ether of which polyhydric alcohol; A methanol, ethanol, Ketones [such as an alcohols; acetone,], such as propanol and a butanol; A tetrahydrofuran, Ether, such as a dioxane; there are lactams, such as lactone; 2-pyrrolidones [such as ester; gamma-butyrolactone,], such as ethyl acetate, sulfolanes, and N-methyl pyrrolidone, and a 1-methyl-2-pyrrolidone. Although an organic solvent gives useful properties, such as shortening of the drying time, reduction of bleeding, and increase of permeability, to an ink constituent, generally (the auxiliary solvent matter defined as this specification is a difference), optical density, the stability of a constituent, or printing quality is not improved. 1,5-pentanediol, 1, 6-hexandiol, 1, 7-heptane diol, n-propanol, and such mixture are in a desirable organic solvent especially.

[0050] The component of the last required to use it with the constituent of this invention is auxiliary solvent mixture, and occupies about 10% - about 20% most preferably about 5% to about 30% 5% - about 40% of abbreviation of the last constituent. This auxiliary solvent mixture contains 1 which is the first component, 3-propanediol, 1, 4-butanediol, or these intermixing-of-material objects. Among these, 1 and 3-propanediol is desirable. Furthermore, the polyethylene-glycol type compound which is the second component, the condensation product of a polyol and an oxidization alkylene, or the mixture of these compounds is also contained. the 2nd component used for this auxiliary solvent mixture - molecular weight - about 200- about 3,400 - it is the mixture of about 200 - about 600 polyethylene glycol or a polyethylene glycol, and a polypropylene glycol preferably Polyethylene glycols (PEG) are desirable and especially the polyethylene glycol that has about 400 molecular weight is desirable. The 2nd component of an auxiliary solvent may be a condensation product of a polyol and an oxidization alkylene which has the following formula.

[0051]

[Formula 15]



[0052] the inside of a formula, and x - H, or CH₃ and R - the alkyl group of H, C₁-C₄, or -CH₂O (CH₂CH₂O) -- eH, b₀ or 1, and a+d+f (c+e) - about 2 - about 100 f - about 1- it is about 6

[0053] The condensation product of a useful polyol and a useful oxidization alkylene is a resultant of a polyol and an oxidization alkylene in this invention. These are indicated by the U.S. Pat. No. 5,180,425 specification of January 19, 1993 and matric (Matrick) appended to this specification as reference. Solubility [usually as opposed to water in these compounds] is about 4.5% (4.5 sections [as opposed to / the water 100 section / Namely,]) at least at 25 degrees C. The oxidization alkylene used for these compounds is the mixture of an ethyleneoxide, a propylene oxide, or both oxides. Although the mixture of the compound with which the degrees of oxy-alkylation differ is produced by the reaction with a single oxidization alkylene, the shown structure is based on the average composition containing a series of oxidization alkylene units. The random and block copolymer of a propylene oxide and an ethyleneoxide can be used. The oxidization alkylene and the polyol which reacted may have three or more hydroxyl groups. Useful triol is a glycerol, a trimethylol propane, and trimethylolethane. Other triol, such as 1, 2, and 4-butane triol and 1, 2, and 6-hexane triol, can be used. Useful tetrols have a pentaerythritol, JI (trimethylol propane), a methyl glucoside, etc. A glucose, a pen toll, etc. can be used. A sorbitol is useful HEKISORU. Other useful HEKISORU has a JIPENTA erythritol and an inositol. Usually, since a condensation product with an oxidization alkylene does not suit pigment dispersion liquid, generally it is not suitable for diols for using it by this invention. One of the exception of the is a condensation product with the oxidization alkylene of neopentyl glycol.

[0054] There are the following in the example of the condensation product of a polyol and an oxidization alkylene.

[0055]

[Table 1]

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表1

製品	R	a + d + f (c + e)	b	f
商標名 Liponic EG-1 ¹⁾	-H	26	0	1
商標名 Liponic SO-20 ¹⁾	-H	20	0	4
商標名 Photonol PHO-7149 ²⁾	-C ₂ H ₅	2.7	1	1
商標名 Photonol PHO-7155 ²⁾	-C ₂ H ₅	7.4	1	1
商標名 Voranol 230-660 ³⁾	-CH ₃	3.0	1	1
商標名 Voranol 234-630 ³⁾	-C ₂ H ₅	3.0	1	1
商標名 Fomrez T-279 ⁴⁾	-C ₂ H ₅	3.1	1	1
商標名 Fomrez T-315 ⁴⁾	-C ₂ H ₅	4.1	1	1

¹⁾ リポ・ケミカルズ・カンパニー、パターソン、N. J.

²⁾ ヘンケル・コーポレーション、アンブラー、P. A.

³⁾ ダウ・ケミカル・カンパニー、ミッドランド、M. I.

⁴⁾ ウィトコ・コーポレーション・オーガニック・デヴィジョン、ニューヨーク、N. Y.

[0056] The condensation product of a polyol and an oxidization alkylene especially desirable although it is used by this invention is above Liponic. It is EG-1. This material has the name of CTFA of GURISERESU -26, is what added the 26-mol ethyleneoxide to the glycerol, and is marketed from a RIPO Chemicals company, Paterson, and New Jersey.

[0057] The first of auxiliary solvent mixture and the second component exist by the weight ratio (the first component : the second component) of about 70:30 - abbreviation 30:70. the weight ratio of a PEG:diol optimal when auxiliary solvent mixture contains a polyethylene-glycol (PEG) type compound and either of 1 and 3-propanediol or 1, and 4-butanediol -- about 50:50- it is about 70:30 The condensation product optimal when auxiliary solvent mixture contains the condensation product of a polyol and an oxidization alkylene with 4[1 and 3-propanediol or 1, and]-butanediol: Diol ratios are about 30:70 - abbreviation 50:50. The ratio of the general most desirable assistant solvent mixture is about 50:50.

[0058] In order to manufacture such a constituent, you may prepare the ink constituent of this invention by what method learned for this industry. The important point of this constituent is that a pigment and a polymer dispersant form stable dispersion liquid in an aqueous carrier and an auxiliary solvent mixture. By one method, a polymer dispersant is first mixed with a pigment. Next, the obtained mill base is ground with a grinding machine, and a particle is decreased to permission particle size. Next, this material is mixed with other ink components and water, and the ink of predetermined concentration is obtained. A surfactant can be added by request, distribution of a pigment can be raised, the surface tension of ink can be changed, and osmosis on paper can be controlled. There are non-ionicity, amphoterism, and an ionic surfactant in a suitable surfactant. In order to acquire the advantage from which other additives, for example, a destruction-of-life agent, the wetting agent, the chelating agent, the viscosity controlling agent, etc. were known for this industry, it can add to this ink constituent by the operating concentration established in this industry.

[0059] By the method of generating the pigment ink for ink jets, it is required to usually decrease the size of a particle using a grinding mill. As for the preservation life of ink, it is desirable that it is two years or more, and it is desirable to choose particle size from which the preservation life of such ink is acquired about the particle size of a pigment. Such a particle size is obtained by shearing a pigment particle using a small tumbling media. Stainless steel, a zirconium silicate, a zirconium oxide, and the spherical particle of glass are contained in the typical medium used

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for manufacture of pigment ink. It may wear out, and may mix into ink dispersion liquid, and the particle with the large surface area used at this trituration process may pollute the last prescription. Although this contamination is based also on a kind and an amount, it may have a bad influence on the property of ink. For example, the stability fall of the ink function to lead etc. may produce the change of pH by reacting by contamination with discoloration of color pigment prescription (especially light color, such as yellow), and the chemicals of prescription of a medium, the difficulty of ink filtration, and the useful life longevity of a printing cartridge. A desirable tumbling media is a high-density spherical ceramic particle of a high degree of hardness which has a smooth and uniform front face highly. In order to use it for manufacture of the ink of this invention, especially a desirable tumbling media is a material which Japanese ***** business manufactures and SE Firestone ASOSHIETSU (S. E. Firestone Associates) of Philadelphia is marketing under the name of a YTZ ceramic bead. This material is the spherical ceramic particle which carried out yttrium processing of the core of the zirconium oxide of a high grade, and raised abrasion resistance. It has a very smooth and uniform front face, and this particle is a perfect globular form and a degree of hardness is [density is 6.0 g/cm³ and] 91. The example of the process of such a material is indicated by the open JP,57-191234,A specification and the JP,56-145118,A specification of November 11, 1981 public presentation on November 25, 1982 appended to this specification as reference.

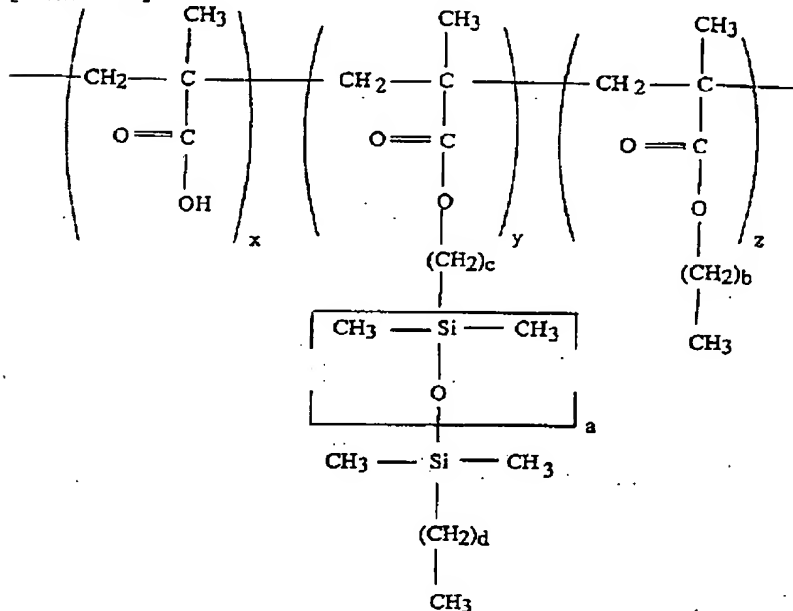
[0060]

[Example] The following example shows manufacture and the usage of the ink constituent of this invention in detail. These detailed explanation is within the limits of the above-mentioned still more general explanation, and illustrates this. These examples are only the purposes of explanation and do not limit the range of this invention.

[0061] The polymer dispersant (it is hereafter described as "the ternary polymerization object L") which has the following general formula was used for the ink constituent of example 1 this invention.

[0062]

[Formula 16]



[0063] (1) The manufacture ternary polymerization object L of the ternary polymerization object L was generated as follows. 22.8g (265 millimole) of methacrylic acids, Poly dimethylsiloxane (PDMS-MA) 7.84g which has a monochrome metacryloxy propyl group in an end group (8.7 millimole) Molecular weight 900, stearyl methacrylate 2.95g (8.7 millimole), Dodecane thiol 2.06g (9.9 millimole), dimethyl-2,2'-azobisisobutyrate 0.64g (2.84 millimole), And after deaerating an isopropyl alcohol 100ml solution with an argon (the process filled up with an argon in part using the Firestone bulb after exhaust air [Firestone Valve] is repeated), it was heated at 70 degrees C for 16 hours. It added gradually, stirring to a 1.0l. hexane at high speed, after cooling this mixture to a room temperature. Filtration under reduced pressure of the obtained solid-state was carried out, it dissociated, and overnight dryness was carried out at 80 degrees C into the vacuum. Reaction yield was about 85%. Protons NMR and GPC determined the property of this copolymer.

[0064] The undiluted solution of a dispersant was generated as follows. 400ml beaker into which 40g of deionized water was put was laid on the hot plate with a magnetic stirrer. After adding into a beaker, stirring ternary polymerization object L12g, 18g of KOH solutions was added to this 20%. This mixture was heated at 50 degrees C for 2 hours. When there was need, the KOH solution was added 20% and pH was adjusted to 7.5. Next, deionized water was added and the above-mentioned undiluted solution weight was set to 100g (ternary polymerization object L12%).

[0065]

(2) Prescription of the mill base (a) mill base prescription A A component Amount Carbon black (Cabot Corp., MONAKU 800) 26.0g Ternary polymerization object L undiluted solution 54.0g Deionized water 100.0g (b) mill base

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prescription B Component Amount Carbon black (Degussa AG and SUPESCHARU black 4A) 26.0g Ternary polymerization object L undiluted solution 54.0g Deionized water 100.0g [0066] The mill bases A and B were prescribed as follows. It front-mixed by stirring a component mechanically until a lump disappears beforehand. This mixture was distributed at the rate of 700rpm with the SHIEGUBARI (Szegvari) grinding machine model 01std type with a zirconium-silicate shot of 10-12 meshes. Although usually carried out for at least 1 hour, this grinding process has temperature controlled and can also be performed more for a long time. The obtained trituration mill base was picked out from the grinding machine, deionized water was added, and the last solid content was made 12%.

[0067] The dispersion liquid which described the mill base prescription A were used, and the ink constituent which has the following component was prepared.

Carbon black 4% (weight)

Ternary polymerization object L 1% Polyethylene glycol (molecular weight 400) 10% 1, 3-propanediol 10% Deionized water 75% [0068] The ink constituent was prepared in the following procedure.

(1) Deionized water, PEG and 1, and 3-propanediol was mixed for 20 minutes.

(2) It added into the above-mentioned mixture, stirring the ground mill base (mill base prescription A). Stirring was continued for 20 minutes.

(3) The 20%KOH solution was added and pH of a constituent was adjusted to 8.3.

(4) It filtered by 1.2 micrometer.

[0069] This ink was used by the ink jet printer, and when it printed and examined on six typical kinds of different papers, a good maintenance property, good optical density, and the desirable advanced printing property were shown.

[0070] The ink constituent which has the following component using the mill base prescription B and the process of a publication in the example 2 example 1 was prepared.

Carbon black 3% Ternary polymerization object L 0.75% Polyethylene glycol (molecular weight 400) 14% 1, 3-propanediol 6% Deionized water This ink is used by the ink jet printer 76.25%, and it prints on six typical kinds of different papers. When it examined, good optical density, the good maintenance property, and the desirable advanced printing property were shown.

[0071] The ink constituent which has the following component using the mill base prescription A and the process of a publication in the example 3 example 1 was prepared.

Carbon black 3% Ternary polymerization object L 0.75% Polyethylene glycol (molecular weight 400) 10% 1, 3-propanediol 10% Deionized water When this ink is used by the conventional ink jet printer 76.25%, a good maintenance property is shown, and it is good optical density. The printed matter in which a series of desirable advanced printing properties are shown was obtained.

[0072] The ink constituent which has the following component using the mill base prescription B and the process of a publication in the example 4 example 1 was prepared.

Carbon black 3% Ternary polymerization object L 1% Brand name Liponic EG-1 10% 1, 3-propanediol 10% Deionized water If this ink is used by the conventional ink jet printer 76%, a good maintenance property will be shown and it will print on six kinds of typical papers. When it examined, the outstanding (good optical density is included) printing property was shown.

[0073] The ink constituent which has the following component using the mill base prescription B and the process of a publication in the example 5 example 1 was prepared.

Carbon black 3% Ternary polymerization object L 0.75% 1, 3-propanediol 10% Polyethylene glycol (molecular weight 400) 10% Deionized water If this ink is used by the ink jet printer 76.25%, a good maintenance property will be shown and it will print on six kinds of typical papers. When it examined, good optical density was shown.

[0074] The ink constituent which has the following component using the process of a publication in the example 6 example 1 was prepared.

carbon black (FW18, Degussa AG, the Ridgefield park, N.J.) 3% Ternary polymerization object L 0.75% 1, 3-propanediol 10% Polyethylene glycol (molecular weight 400) 10% Deionized water If this ink is used by the conventional ink jet printer 76.25%, a good maintenance property will be shown and it will print on six kinds of typical papers. When it examined, good optical density was shown.

[0075] The ink constituent which has the following component using the process of a publication in the example 7 example 1 was prepared. Carbon black (FW18) 3% Ternary polymerization object L 0.75% 1, 3-propanediol 10% Brand name Liponic EG-1 10% Brand name Kathon PFR (a destruction-of-life agent, loam & Haas) 0.15% Deionized water If this ink is used by the conventional ink jet printer 76.10%, a good maintenance property will be shown and it will print on six kinds of typical papers. When it examined, good optical density was shown.

[0076] The ink constituent which has the following component using the process of a publication in the example 8 example 1 was prepared.

Carbon black (SUPESCHARUBURAKU4A) 3% Ternary polymerization object L 0.75% 1, 4-butanediol 10% Polyethylene glycol (molecular weight 600) 10% n-propanol 0.2% Deionized water If this ink is used by the conventional ink jet printer 75%, a good maintenance property will be shown and it will print on six kinds of typical papers. When it examined, good optical density was shown.

[0077]

[Effect of the Invention] Since the pigment ink constituent for ink jet printers of this invention contains a specific auxiliary solvent system, it shows the property which was excellent in points, such as an improvement of the blinding

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of stability, optical density, viscosity, a printing property (reduction of running of feathering in water resistance, lightfastness, and a printing page and ink), and the printer jet at the time of printer un-using it.

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TECHNICAL FIELD

[The technical field to which invention belongs] this invention relates to the ink constituent used for an ink jet printer.

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PRIOR ART

[Description of the Prior Art] Ink-jet printing is performed by injecting ink from a nozzle to paper or other print media. Ink can be made to inject by various kinds of methods towards a medium. For example, in electrostatic printing, ink is injected by the electrostatic field towards a medium from a nozzle. In the procedure of other ink-jet printings known as a squeeze tube, the piezoelectric device is used into an ink nozzle. Ink is transported to print media through a nozzle by the electric distortion of a piezoelectric device. In the procedure of other ink-jet printings in which thermal ** is known as bubble ink-jet printing, when the bubble of a gaseous phase expands within a nozzle, ink is injected towards print media from a nozzle. The print processes of these various kinds are indicated by issue (refer to Chapter 13 "ink-jet printing (Ink Jet Printing)" especially) in DABEKKU (Durbeck) and edited by Shache (Sherr) "hard copy output unit (Output Hard Copy Devices)", and Academic Press (Academic Press) 1988.

[0003] The ink constituent used for an ink jet printer usually contains the organic solvent of deionized water, water solubility, or water and compatibility, and a coloring agent. Generally, a coloring agent is the color of fusibility. There are many problems [the chemicals-proof nature with low thermal stability whose printing quality is not good is low and] of being easy to oxidize including bleeding, feathering, etc. of ink which plugging produces in an injection channel by the evaporation of a solvent which is not [with low water resistance] good, or change of the solubility of a color and which a color crystallizes in the ink [it is regrettable and] which contains a fusibility color especially.

[0004] Many of these problems are solvable by using an insoluble pigment instead of the fusibility color used for ink prescription. Generally, the pigment is excellent in the property as compared with the color, and excellent in respect of the ability to also suit especially water resistance, lightfastness, thermal stability, oxidation stability, and the paper coated or processed also at a regular paper. However, in order not to dissolve in an ink constituent, therefore to make it distribute, some new problems produce a pigment. The stability of ink is very important for maintaining the homogeneity of a property, and a row in the point of making it both not get a pigment blocked in an ink jet, while not using it. It is ideal to make the amount of a pigment required in an ink constituent, of course into the minimum from the reason of both stability and cost. However, if the amount of the pigment in an ink constituent is reduced, the optical density of a picture will fall. Furthermore, in order to secure required stability, while the balance of composition is required, therefore has suitable viscosity in an ink jet printer using a constituent, when it prints on paper, it is important [water resistance and lightfastness are good, and] that running and feathering are also the minimum. It was very difficult to develop ink prescription which optimized all of these properties until now. Adjusting the dispersant and solvent system of an ink constituent for the purpose of maintaining and optimizing the balance of these properties that conflict in many cases as common practice was performed. However, prescription which optimized all these properties, without using a specific polymer dispersant before this invention was not attained.

[0005] The ink constituent for ink jets which contains the auxiliary solvent of a water carrier medium, pigment dispersion liquid, and a polyol and an oxidation alkylene in the U.S. Pat. No. 5,180,425 specification of the matric (Matrick) on January 19, 1993 is indicated. The life of ink jet printer ability is lengthened and these ink is taught that there is coat-proof formation nature. RAIPO nick (Liponic) EG-1 is one of the indicated desirable auxiliary solvents. The polyethylene glycol is contained in other solvents used for this patent.

[0006] Pigment dispersion liquid, the water carrier medium, and a polyol, the condensation product of an oxidation alkylene and the ink constituent containing the auxiliary solvent mixture containing a cyclic-amide derivative for ink jets are indicated by the U.S. Pat. No. 5,302,197 specification of wick Lamaism NAIKE (Wickramanayke) on April 12, 1994. It is taught that RAIPO nick EG-1 is useful as a condensation-product component of a polyol and an oxidation alkylene.

[0007] A water carrier medium, a specific alkyl polyol ether auxiliary solvent, and the ink for ink jets that consists of pigment dispersion liquid (what stabilized the pigment particle with the dispersant) are indicated by the Europe patent No. 603,469 application of Chillan and others on June 29, 1994 (Chan). It is taught that these ink has viscosity, surface tension, plugging prevention of a nozzle, printing quality, light stability, bleeding-proof nature, and waterproof good balance. 1, 2, and 3-butane triol is contained in the solvent used by invention of an indication.

[0008] A clear image is formed in the U.S. Pat. No. 4,597,794 specification of OTA and others on July 1, 1986, and ink prescription used for the ink-jet printing process said to have a good physical property is indicated. A polyethylene glycol and 1, 2, and 6-hexane triol are contained in the solvent indicated especially in order to use it for this ink.

[0009] Giving characteristic mixture, when optimizing a property was found out by using the specific auxiliary solvent mixture which contains 1 and 3-propanediol or 1, and 4-butanediol with either the polyethylene glycol of (a)

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low molecular weight, a related compound or the condensation product of the (b) polyol and an oxidization alkylene for the water-color-ink constituent containing the dispersion liquid of an insoluble pigment. That is, the property these constituents excelled [property] in stability, optical density, viscosity, the printing property (running of feathering in water resistance, lightfastness, and the printed page and ink is the minimum), and the row in points, such as a problem (the blinding of the printer jet at the time of printer un-using it is the minimum) of printer maintenance, (even when low pigment concentration is used) is acquired. About the combination of the specific auxiliary solvent shown by this invention, neither a publication nor suggestion has each in the above-mentioned patent.

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EFFECT OF THE INVENTION

[Effect of the Invention] Since the pigment ink constituent for ink jet printers of this invention contains a specific auxiliary solvent system, it shows the property which was excellent in points, such as an improvement of the blinding of stability, optical density, viscosity, a printing property (reduction of running of feathering in water resistance, lightfastness, and a printing page and ink), and the printer jet at the time of printer un-using it.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] Therefore, the purpose of this invention is to offer the pigment ink constituent with which it has been improved for [containing a specific auxiliary solvent system] ink jet printers.

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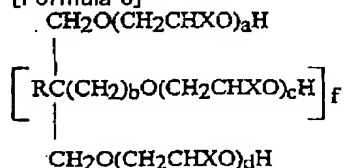
MEANS

[Means for Solving the Problem] Other purposes and features of this invention become clear by the following indication.

[0012] In the 1st mode of this invention, the pigment of 1 % of the weight - about 10 % of the weight of (a) abbreviation, (b) About 0.1 % of the weight - about 10% of the weight of the polymer dispersant for the above-mentioned pigments, the water carrier of 50 % of the weight - about 93 % of the weight of (c) abbreviation, and (d) (1) 1 and 3-propanediol or 1, and 4-butanediol, (2) The water-color-ink constituent containing about 5% - about 40% of auxiliary solvent mixture containing the matter chosen from the following (i) - (iii) a group suitable for use of an ink jet printer is offered. (i) Condensation product of the polyethylene glycols which have about 200 - about 3,400 molecular weight, the polyol which has the mixture of polyethylene glycols and polypropylene glycols, and the formula of (ii) following in a row, and a polyacid-ized alkylene.

[0013]

[Formula 8]



[0014] the inside of a formula, and X — H, or CH₃ and R — the alkyl group of H, C₁-C₄, or CH₂O (CH₂CH₂O) — eH, b₀ or 1, and a+d+f (c+e) — about 2 - about 100 f — about 1- it is about 6 (iii) Such mixture. In addition, above-mentioned (1) ratio [of : (2) / weight] (1): (2) is about 70:30 - abbreviation 30:70.

[0015] The 2nd mode of this invention is related with the auxiliary solvent mixture shown above (d).

[0016] The percentage and the ratios which were used for this specification are "weight %" and a "weight ratio", unless it otherwise specifies. The molecular weight used for this specification is number average molecular weight, unless it otherwise specifies.

[0017]

[Embodiments of the Invention] this invention relates to the water-color-ink constituent suitable for using it for an ink jet printer. These constituents contain the polymer dispersant (a pigment and a dispersant exist in the constituent as dispersion liquid), the water carrier, and the specific auxiliary solvent mixture for an insoluble pigment and a pigment. Each of these required components is explained in detail below with some additional components.

[0018] a polymer dispersant — the constituent of this invention — setting — about 0.1% - about 10% of the last component — it is contained about 0.5% to about 4% most preferably about 0.25% to about 5% both the anion nature by which it is known for the industry that it is suitable for using it for the polymer dispersant suitable for using it by this invention as a dispersant of the ink manufacture object for ink jets cation nature and a non-ionicity polymer — although — it is contained The example of such a material is indicated by the U.S. Pat. No. 5,310,778 specification of Shore and others on May 10, 1994 appended to this specification as reference (Shor). A homopolymer, a copolymer, the letter polymer of branching, or a graft polymer is sufficient as such a polymer dispersant. Moreover, a random polymer or a block polymer is sufficient.

[0019] The block copolymer of AB, BAB, and ABC is one sort of a polymer dispersant useful to this invention. Desirable things are AB and BAB which were guided from at least one sort of alkyl acrylics or a methacrylic ester and an amine substitution acrylic, or the monomers of a methacrylic ester, and an ABC block copolymer. MA [on February 4, 1992 when desirable AB and BAB block copolymers, and these processes were appended to this specification as reference] (— it is indicated by the U.S. Pat. No. 5,085,698 specification of Ma) and others

[0020] A polymer dispersant useful to operation of this invention usually tends to combine a hydrophobic segment with the pigment particle in an ink constituent including both polymer segments of a hydrophobic property and a hydrophilic property, it is tended by the liquid ink medium to carry out the solvation of the hydrophilic segment, and it stabilizes dispersion liquid according to these, a three-dimensional mechanism, and/or an ionicity mechanism.

[0021] The desirable polymer dispersant of a kind used by this invention contains the block or graft copolymer containing a hydrophilic polymer segment and the hydrophobic polymer segment which contains a stable siloxyl substituent to hydrolysis. Especially a desirable thing is a graft copolymer containing a hydrophilic polymer segment (especially acrylate or a methacrylate copolymer) and the hydrophobic polymer segment guided from the

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[0022]

$$\text{R}-\text{Si}(\text{R})_2-\text{O}-\left[\text{Si}(\text{R})_2-\text{O}\right]_n-\text{Si}(\text{R})_2-\text{R}$$

[0024] The desirable polymerization nature powder of other kinds is a graft copolymer containing the hydrophobic polymer segment which has about 1,500 – about 20,000 molecular weight, has a stable siloxyl substituent to (a) hydrophilic-property polymer segment and (b) hydrolysis, and has about 400 – about 3,000 molecular weight, and the stabilization segment chosen from the group which becomes a row from the surface activity macromolecule object of (c) reactivity, a protective colloid macromolecule object, and a non-siloxyl hydrophobic monomer.

[0026] The most desirable thing has the following formula in a principal chain with this kind of polymer dispersant.

[illegible]

[0028] The inside of a formula, 3; x — about 5— about 100 — desirable — about 15 — about 50 y — about 1— about 2 — desirable — about 1 z — about 1— about 5 — desirable — about 1 —;a — about 3— about 45 — desirable — about 9 b — about 3— about 29 — desirable — about 15 — about 17 c — about 2— about 8 — desirable — about — d — 0— about 7 — it is about 3 preferably In addition, it is within the limits of this invention which all the structural units expressed with x, and y and z are distributing at random in the principal chain of a polymer. These polymer

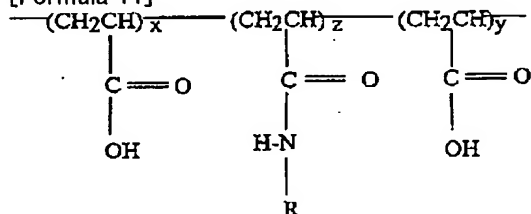
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dispersants are indicated by the U.S. patent application "the polymer dispersant for pigment use ink" of ***** of the beaches (Beach) appended to this specification as reference. The end group of the dispersant of this invention is not limited. For the purpose of explanation, it is contained like [a thio substitution hydrocarbon] hydrogen.

[0029] The polymer dispersant of other kinds is indicated by the U.S. patent application 08th/No. 360,200 specification of December 21, 1994 and beaches (Beach) appended to this specification as reference. These matter is the graft polymers containing the hydrophobic segment side chain which has one side chain combined with one principal chain as preferably as the principal chain of the hydrophilic polyacrylic acid of the weight average molecular weight of about 1,000 - about 5,000 between. This kind of desirable polymer has one of the following structure expressions in a principal chain.

[0030]

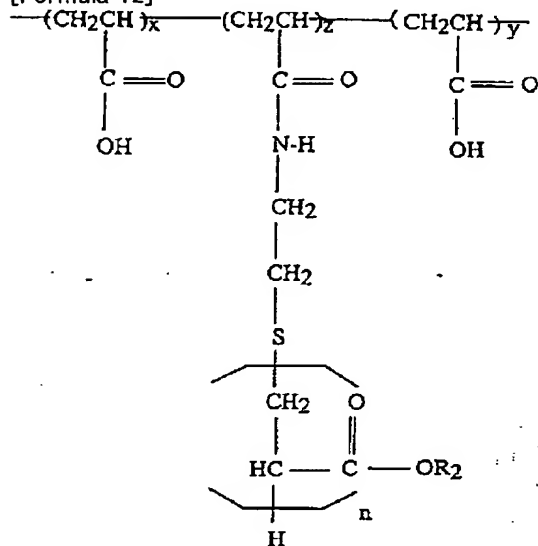
[Formula 11]



[0031] x+y is [about 1 - abbreviation 10, and R of about 20 - about 200 z] the alkyl group of C6-C36, or the following R1 among a formula. R1 is the alkyl group or the following basis of C4-C20.

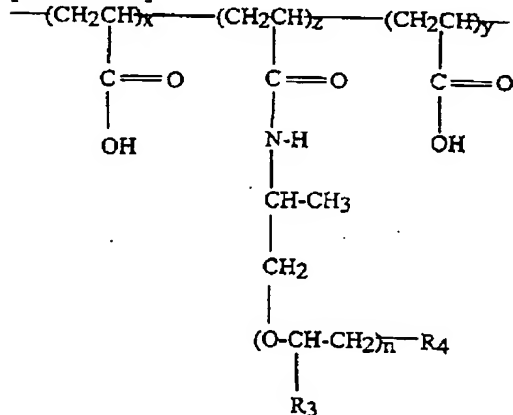
[0032]

[Formula 12]



[0033] the inside of a formula, and x+y --- about 20 - about 200 z --- about 1 - about 10 n --- about 2- about 40 and R2 --- an alkyl group or an aryl group --- desirable --- a butyl --- or [0034]

[Formula 13]

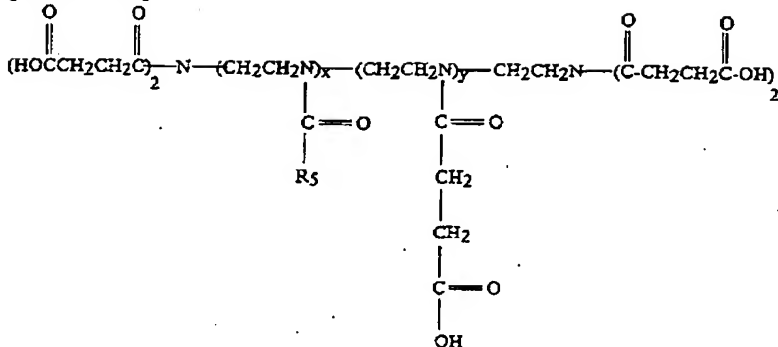


[0035] In about 1 - abbreviation 10, and R3, H, or CH3 and R4 have OCH3, and H, CH3, or n has [the inside of a formula, and x+y / about 20 - about 200 z] about 10 - abbreviation 60, or the following formula.

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[0036]

[Formula 14]



[0037] y of about 6 - Abbreviation 20 and x is [about 1 - abbreviation 5, and R5] the alkyl groups of C6-C30 among a formula.

[0038] The graft copolymer dispersant of this invention is low molecular weight comparatively, in order to acquire the stability of a particle, and its viscosity needs to be low in order to use it for the stable ink for ink-jet printing. For this reason, the polar-solvent polymerization method for generating a copolymer is chosen. The molecular weight of a copolymer and homogeneity are controlled by such method by maintaining the solubility of not only the copolymer obtained but all start raw materials (it is a chain transfer agent to a free radical initiator, a hydrophobic property and a hydrophilic monomer, and a row). In order to write a prescription to ink-jet printing and to make a water medium suspend the compounded copolymer, it needs to collect copolymers from the polar organic solvent in reaction mixture, and it is necessary to make it dissolve them in water. The copolymer recovery method from a typical polar polymerization solvent includes the following processes.

1. The solution of a copolymer is added to non-solvents, such as a hexane, a polymer is settled from a solution, this refines a copolymer, vacuum filtration of the 2. precipitate is carried out, and 3. copolymer precipitate is dried.

[0039] Next, copolymer powder can be dissolved in an aqueous base and it can be used for generation of the ink for ink-jet printing. This method has high cost and is superfluously complicated. [of cost]

[0040] The desirable method for collecting the dispersants of a copolymer from a polar organic polymerization solvent improves printing quality which decreases it not only merely collects the dispersants of a copolymer, but that the ink-jet ink generated from these dispersants forms a satellite and a splatter. Specifically, these desirable methods include the following process.

1. Dissolve in an aqueous base and exchange 2. solvent, after evaporating a solvent.

[0041] At solvent evaporation and a dissolution process, vacuum tray dryness, rotation evaporation dryness, drum dryness, a turning-circle cylinder vacuum drying, or spray drying evaporates a polar solvent from a copolymer first by the standard method of changing the solution of a copolymer into dryness powder. Next, the dry copolymer powder is dissolved in a water base, and it enables it to use it for generation of the ink of the pigment for ink jets.

[0042] a solvent exchange-buffering-method process — about 35% — about 60% of the polar solvent in a polymerization reactor (preferably about 50%) — distillation — removing — deionized water and an aqueous base (for example, KOH solution) — adding — pH — about 4.5 — about 6.5 — it adjusts to about 5 preferably In order for the boiling point to make a solvent distill from water until all polar solvents amount to about 100 degrees C from which temperature is removed in the case of a low polar solvent, the temperature of this mixture is raised slowly. (This process cannot be used when the boiling point of a polar solvent is higher than the boiling point of water.) further — an aqueous base (for example, KOH solution) — this solution — in addition, pH — about 7 — about 8.5 — about 7.5 is raised preferably Subsequently, this solution is used for prescription of the pigment ink for ink jets.

[0043] The 2nd component of the ink constituent of this invention is a pigment which is an insoluble coloring agent. the constituent of this invention — a pigment — the last constituent — receiving — about 0.1% — about 10% — about 0.5% — 4% exists most preferably about 0.25% to about 5% Actually, one of the important advantages of this invention enables prescription of ink which has low pigment concentration (for example, 0.5 — 4%), and moreover, it is quality and is offering the outstanding optical density. February 4, 1992 and MA (appended to this specification as reference as a pigment useful to operation of this invention — all of the well-known conventional pigment can be used in this industry that is indicated by the U.S. Pat. No. 5,085,698 specification of Ma) and others Even if it uses it independently, you may use a pigment, combining.

[0044] The particle of a pigment needs to have [an ink-jet printer, especially a diameter] small ink enough so that the inside of the injection nozzle which is usually about 10 micrometers — about 50 micrometers can be flowed freely. Particle size affects the distributed stability of an important pigment through the life of ink again. The Brownian motion of a particle is useful to condensation prevention of a particle, and, thereby, a product is stabilized further. A useful size range is about 0.05 micrometers — about 15 micrometers. The range of the particle size of a pigment is about 0.05 micrometers — about 5 micrometers, and the range of it is about 0.05 micrometers — about 1 micrometer most preferably. A pigment can be used also with the gestalt which carried out [the dry gestalt or] humidity. For example, a pigment is usually manufactured in an aqueous medium and is obtained as a filter press cake containing water. With the gestalt of this filter press cake, a pigment is not condensed like [in the case of a

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dryness gestalt]. Therefore, the pigment of the gestalt of the filter press cake containing water does not need to perform solution condensation in the manufacturing process of ink like [at the time of using the dry pigment].

[0045] The particle of a metal or a metallic oxide can also be used for operation of this invention. For example, the metal and the metallic oxide are suitable for manufacture of the ink for magnetic ink jets. The oxide of a particle, for example, a silica, an alumina, a titania, etc. can be used. Furthermore, the pulverized metal particles, for example, copper, iron, steel, aluminum, and alloys can be chosen because of a suitable use.

[0046] there are inorganic pigments, such as organic pigment; titanium oxide, such as color lake; nitroglycerine pigments, such as polycyclic formula pigment; basic dye lakes, such as azo pigment; phthalocyanine pigments, such as an azo lake, a disazo condensation pigment, and a chelate azo pigment, a perylene pigment, an anthraquinone pigment, a Quinacridone pigment, a dioxazine pigment, a thio indigo pigment, an isoindolinone pigment, and a kino. FUTARON pigment, and an acid-dye lake, an oximido pigment, an aniline black, and a daylight fluorescent pigment, an iron oxide, and carbon black, etc. in the example A desirable pigment contains titanium oxide, an iron oxide, and carbon black in using it in this invention. For the example of the available pigment of marketing which can be used in this invention Brand name Heliogen Blue L 6901F (BASF), Brand name Heliogen Blue NBD 7010 (BASF), Brand name Heliogen Blue K 7090 (BASF), Brand name Heucophthal Blue GXBT-583D (HYU back), Brand name Irgalite Rubin 4BL (Ciba-Geigy), Brand name Quindo A Magenta (Mobey), brand name Indofast Brilliant scarlett (Mobey), Brand name Hostaperm Scarlett GO (Hoechst), Permanent Rubin F6B (Hoechst), brand name Monastral Scarlett (Ciba-Geigy), Brand name Raven 1170 (COL KEMU), SUPSSHARU black 4A (Degussa AG), Black FW18 (Degussa AG), brand name Sterling NS Black (Cabot), Brand name Sterling NSX 76 (Cabot) Monarch 880 (Cabot), Brand name Tipure R-101 (E. I. du Pont de Nemours), MOGARU L (Cabot), BK 8200 (pole URITCHI) Brand name Heliogen Green K 8683 (BASF), Brand name Heliogen Green L9140 (BASF), Brand name Monastral Red B (Ciba-Geigy), brand name Monastral Violet R (Ciba-Geigy) Brand name Hostaperm Orange GR (Hoechst), brand name Paliogen Orange (BASF), L75-2377 Yellow (Sun KEMU) and L74-1357 Yellow (Sun KEMU), Brand name Hostaperm Yellow H4G (Hoechst), brand name Argazin Yellow 5GT (Ciba-Geigy), Permanent Yellow G3 R-01 (Hoechst), brand-name Novoperm yellow FGL (Hoechst), Brand name Chromophthal Yellow 3G (Ciba-Geigy), HANZA Yellow X (Hoechst), brand name Dalamar Yellow YT-858-D (HYU back), HANZA Brilliant Yellow There is 5GX-02 (Hoechst) etc.

[0047] The 3rd component of the ink constituent of this invention is a water carrier medium. This component is the mixture of water (preferably deionized water) or water, and at least one kind of water-soluble organic solvent. a water carrier component — constituent [of this invention / about 50% of] — about 70% — about 80% exists preferably about 93% Selection of suitable mixture is dependent on the kind of paper in which ink is printed by the drying time required for the requirements for the specific ink prescribed, for example, desirable surface tension, viscosity, the pigment to be used, and pigment ink, and the row etc. As an example of representation of the water-soluble organic solvent which can be chosen (1) Methyl alcohol, ethyl alcohol, n-propyl alcohol, Isopropyl alcohol, n-butyl alcohol, sec-butyl alcohol, t-butyl alcohol, isobutyl alcohol, furfuryl alcohol, Alcohols; (2) acetones, such as a tetrahydrofurfuryl alcohol, Ketones or keto-alcohols; (3) tetrahydrofurans, such as a methyl ethyl ketone and diacetone alcohol, Ether; (4) ethyl acetate, such as a dioxane, an ethyl lactate, an ethylene carbonate, Ester; (5) ethylene glycol, such as a propylene carbonate, a diethylene glycol, A glycerol, the 2-methyl -2, 4-pentanediol, 1 and 2, 6-hexane triol, Polyhydric alcohol, such as a thiodiglycol; (6) ethylene-glycol monomethyl (or monoethyl) ether, The diethylene-glycol monomethyl (or monoethyl) ether, the propylene-glycol monomethyl (or monoethyl) ether, The low-grade alkyl monochrome guided from alkylene glycol, such as the triethylene-glycol monomethyl (or monoethyl) ether and the diethylene-glycol dimethyl (or diethyl) ether, or a diethers; (7) pyrrolidone, a N-methyl-2-pyrrolidone, There are sulfur content compounds, such as nitrogen content cyclic compounds, such as 1 and 3-dimethyl-2-imidazolidinone, (8) dimethyl sulfoxide, and a tetramethylen sulfone. There are lactone and lactams in other useful solvents.

[0048] When using the mixture of water and an organic solvent as a carrier medium by this invention, a medium usually contains 25% of ****, about 75% of organic solvents -, and about 0.1% of 99.9% of **** and organic solvents. Desirable ratios are 50% of ****, about 50% of organic solvents -, and about 0.1% of 99.9% of **** and organic solvents. Such percentage receives the total weight of a water carrier medium. What is used for a water carrier medium in the term of the "organic solvent" used on these specifications should understand that it is not what means that a specific material used as a component of the auxiliary solvent of this invention is included.

[0049] In the desirable organic solvent used for the water carrier medium component of this invention Ethylene glycol, 1 and 2, 6-hexane triol, a thiodiglycol, Polyhydric alcohol, such as a hexylene glycol and a diethylene glycol; Pentanediol, Glycol ethers, such as diols; lauric-acid propylene glycols, such as hexandiol and homologous-series diols; Glycerol; and the ethylene glycol monomethyl (or monoethyl) ether, The diethylene-glycol methyl (or ethyl) ether, the triethylene-glycol monomethyl (or monoethyl) ether, The low-grade alkyl ether of which polyhydric alcohol; A methanol, ethanol, Ketones [, such as an alcohols; acetone,], such as propanol and a butanol; A tetrahydrofuran, Ether, such as a dioxane; there are lactams, such as lactone; 2-pyrrolidones [, such as ester; gamma-butyrolactone,], such as ethyl acetate, sulfolanes, and N-methyl pyrrolidone, and a 1-methyl-2-pyrrolidone. Although an organic solvent gives useful properties, such as shortening of the drying time, reduction of bleeding, and increase of permeability, to an ink constituent, generally (the auxiliary solvent matter defined as this specification is a difference), optical density, the stability of a constituent, or printing quality is not improved. 1,5-pentanediol, 1, 6-hexandiol, 1, 7-heptane diol, n-propanol, and such mixture are in a desirable organic solvent especially.

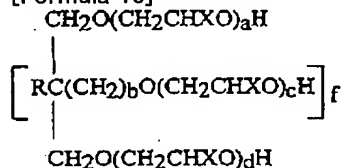
[0050] The component of the last required to use it with the constituent of this invention is auxiliary solvent mixture, and occupies about 10% — about 20% most preferably about 5% to about 30% 5% — about 40% of abbreviation

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of the last constituent. This auxiliary solvent mixture contains 1 which is the first component, 3-propanediol, 1, 4-butanediol, or these intermixing-of-material objects. Among these, 1 and 3-propanediol is desirable. Furthermore, the polyethylene-glycol type compound which is the second component, the condensation product of a polyol and an oxidization alkylene, or the mixture of these compounds is also contained. the 2nd component used for this auxiliary solvent mixture — molecular weight — about 200— about 3,400 — it is the mixture of about 200 — about 600 polyethylene glycol or a polyethylene glycol, and a polypropylene glycol preferably Polyethylene glycols (PEG) are desirable and especially the polyethylene glycol that has about 400 molecular weight is desirable. The 2nd component of an auxiliary solvent may be a condensation product of a polyol and an oxidization alkylene which has the following formula.

[0051]

[Formula 15]



[0052] the inside of a formula, and x — H, or CH₃ and R — the alkyl group of H, C₁-C₄, or —CH₂O (CH₂CH₂O) — eH, b₀ or 1, and a+d+f (c+e) — about 2 — about 100 f — about 1— it is about 6

[0053] The condensation product of a useful polyol and a useful oxidization alkylene is a resultant of a polyol and an oxidization alkylene in this invention. These are indicated by the U.S. Pat. No. 5,180,425 specification of January 19, 1993 and matric (Matrick) appended to this specification as reference. Solubility [usually as opposed to water in these compounds] is about 4.5% (4.5 sections [as opposed to / the water 100 section / Namely,]) at least at 25 degrees C. The oxidization alkylene used for these compounds is the mixture of an ethyleneoxide, a propylene oxide, or both oxides. Although the mixture of the compound with which the degrees of oxy-alkylation differ is produced by the reaction with a single oxidization alkylene, the shown structure is based on the average composition containing a series of oxidization alkylene units. The random and block copolymer of a propylene oxide and an ethyleneoxide can be used. The oxidization alkylene and the polyol which reacted may have three or more hydroxyl groups. Useful triol is a glycerol, a trimethylol propane, and trimethylolethane. Other triol, such as 1, 2, and 4-butane triol and 1, 2, and 6-hexane triol, can be used. Useful tetrols have a pentaerythritol, JI (trimethylol propane), a methyl glucoside, etc. A glucose, a pen toll, etc. can be used. A sorbitol is useful HEKISORU. Other useful HEKISORU has a JIPENTA erythritol and an inositol. Usually, since a condensation product with an oxidization alkylene does not suit pigment dispersion liquid, generally it is not suitable for diols for using it by this invention. One of the exception of the is a condensation product with the oxidization alkylene of neopentyl glycol.

[0054] There are the following in the example of the condensation product of a polyol and an oxidization alkylene.

[0055]

[Table 1]

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表1

製品	R	a + d + f (c + e)	b	f
商標名 Liponic EG-1 ¹⁾	-H	26	0	1
商標名 Liponic SO-20 ¹⁾	-H	20	0	4
商標名 Photonol PHO-7149 ²⁾	-C ₂ H ₅	2.7	1	1
商標名 Photonol PHO-7155 ²⁾	-C ₂ H ₅	7.4	1	1
商標名 Voranol 230-660 ³⁾	-CH ₃	3.0	1	1
商標名 Voranol 234-630 ³⁾	-C ₂ H ₅	3.0	1	1
商標名 Fomrez T-279 ⁴⁾	-C ₂ H ₅	3.1	1	1
商標名 Fomrez T-315 ⁴⁾	-C ₂ H ₅	4.1	1	1

¹⁾ リポ・ケミカルズ・カンパニー、パターソン、N. J.

²⁾ ヘンケル・コーポレーション、アンブラー、P. A.

³⁾ ダウ・ケミカル・カンパニー、ミッドランド、M. I.

⁴⁾ ウィットコ・コーポレーション・オーガニック・デヴィジョン、ニューヨーク、N. Y.

[0056] The condensation product of a polyol and an oxidization alkylene especially desirable although it is used by this invention is above Liponic. It is EG-1. This material has the name of CTFA of GURISERESU -26, is what added the 26-mol ethyleneoxide to the glycerol, and is marketed from a RIPO Chemicals company, Paterson, and New Jersey.

[0057] The first of auxiliary solvent mixture and the second component exist by the weight ratio (the first component : the second component) of about 70:30 - abbreviation 30:70. the weight ratio of a PEG:diol optimal when auxiliary solvent mixture contains a polyethylene-glycol (PEG) type compound and either of 1 and 3-propanediol or 1, and 4-butanediol - about 50:50- it is about 70:30 The condensation product optimal when auxiliary solvent mixture contains the condensation product of a polyol and an oxidization alkylene with 4[1 and 3-propanediol or 1, and]-butanediol: Diol ratios are about 30:70 - abbreviation 50:50. The ratio of the general most desirable assistant solvent mixture is about 50:50.

[0058] In order to manufacture such a constituent, you may prepare the ink constituent of this invention by what method learned for this industry. The important point of this constituent is that a pigment and a polymer dispersant form stable dispersion liquid in an aqueous carrier and an auxiliary solvent mixture. By one method, a polymer dispersant is first mixed with a pigment. Next, the obtained mill base is ground with a grinding machine, and a particle is decreased to permission particle size. Next, this material is mixed with other ink components and water, and the ink of predetermined concentration is obtained. A surfactant can be added by request, distribution of a pigment can be raised, the surface tension of ink can be changed, and osmosis on paper can be controlled. There are non-ionicity, amphoterism, and an ionic surfactant in a suitable surfactant. In order to acquire the advantage from which other additives, for example, a destruction-of-life agent, the wetting agent, the chelating agent, the viscosity controlling agent, etc. were known for this industry, it can add to this ink constituent by the operating concentration established in this industry.

[0059] By the method of generating the pigment ink for ink jets, it is required to usually decrease the size of a particle using a grinding mill. As for the preservation life of ink, it is desirable that it is two years or more, and it is desirable to choose particle size from which the preservation life of such ink is acquired about the particle size of a pigment. Such a particle size is obtained by shearing a pigment particle using a small tumbling media. Stainless steel, a zirconium silicate, a zirconium oxide, and the spherical particle of glass are contained in the typical medium used

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for manufacture of pigment ink. It may wear out, and may mix into ink dispersion liquid, and the particle with the large surface area used at this trituration process may pollute the last prescription. Although this contamination is based also on a kind and an amount, it may have a bad influence on the property of ink. For example, the stability fall of the ink function to lead etc. may produce the change of pH by reacting by contamination with discoloration of color pigment prescription (especially light color, such as yellow), and the chemicals of prescription of a medium, the difficulty of ink filtration, and the useful life longevity of a printing cartridge. A desirable tumbling media is a high-density spherical ceramic particle of a high degree of hardness which has a smooth and uniform front face highly. In order to use it for manufacture of the ink of this invention, especially a desirable tumbling media is a material which Japanese ***** business manufactures and SE Firestone ASOSHIETSU (S. E.Firestone Associates) of Philadelphia is marketing under the name of a YTZ ceramic bead. This material is the spherical ceramic particle which carried out yttrium processing of the core of the zirconium oxide of a high grade, and raised abrasion resistance. It has a very smooth and uniform front face, and this particle is a perfect globular form and a degree of hardness is [density is 6.0 g/cm³ and] 91. The example of the process of such a material is indicated by the open JP,57-191234,A specification and the JP,56-145118,A specification of November 11, 1981 public presentation on November 25, 1982 appended to this specification as reference.

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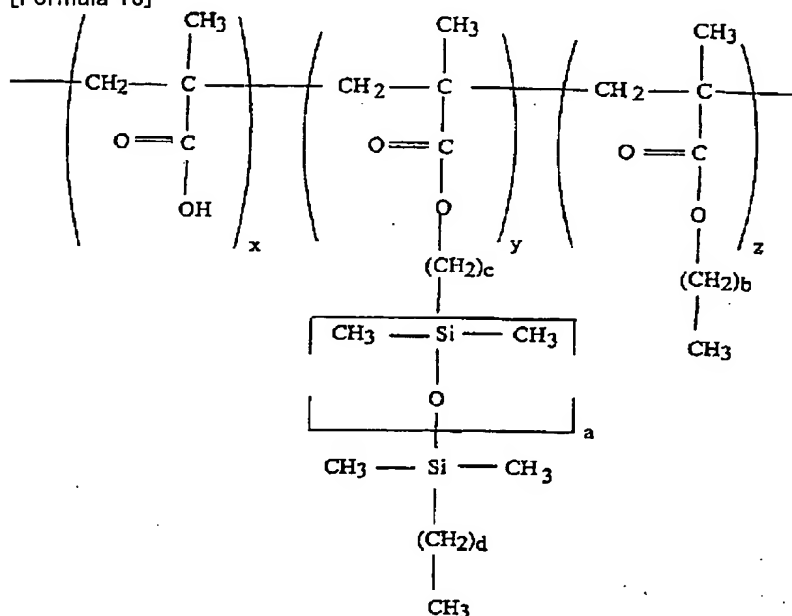
EXAMPLE

[Example] The following example shows manufacture and the usage of the ink constituent of this invention in detail. These detailed explanation is within the limits of the above-mentioned still more general explanation, and illustrates this. These examples are only the purposes of explanation and do not limit the range of this invention.

[0061] The polymer dispersant (it is hereafter described as "the ternary polymerization object L") which has the following general formula was used for the ink constituent of example 1 this invention.

[0062]

[Formula 16]



[0063] (1) The manufacture ternary polymerization object L of the ternary polymerization object L was generated as follows: 22.8g (265mm mol) of methacrylic acids, poly dimethylsiloxane (PDMS-MA) 7.84g (a 8.7mm mol —) which has a monochrome metacryloxy propyl group in an end group Molecular weight 900, stearyl methacrylate 2.95g (8.7mm mol), Dodecane thiol 2.06g (9.9mm mol), dimethyl-2,2'-azobisisobutyrate 0.64g (2.84mm mol), And after deaerating an isopropyl alcohol 100ml solution with an argon (the process filled up with an argon in part using the Firestone bulb after exhaust air [Firestone Valve] is repeated), it was heated at 70 degrees C for 16 hours. It added gradually, stirring to a 1.0l. hexane at high speed, after cooling this mixture to a room temperature. Filtration under reduced pressure of the obtained solid-state was carried out, it dissociated, and overnight dryness was carried out at 80 degrees C into the vacuum. Reaction yield was about 85%. . Protons NMR and GPC determined the property of this copolymer.

[0064] The undiluted solution of a dispersant was generated as follows. 400ml beaker into which 40g of deionized water was put was laid on the hot plate with a magnetic stirrer. After adding into a beaker, stirring ternary polymerization object L12g, 18g of KOH solutions was added to this 20%. This mixture was heated at 50 degrees C for 2 hours. When there was need, the KOH solution was added 20% and pH was adjusted to 7.5. Next, deionized water was added and the above-mentioned undiluted solution weight was set to 100g (ternary polymerization object L12%).

[0065]

(2) Prescription of the mill base (a) mill base prescription A A component Amount Carbon black (Cabot Corp., MONAKU 800) 26.0g Ternary polymerization object L undiluted solution 54.0g Deionized water 100.0g (b) mill base prescription B Component Amount Carbon black (Degussa AG and SUPESCHARU black 4A) 26.0g Ternary polymerization object L undiluted solution 54.0g Deionized water 100.0g [0066] The mill bases A and B were prescribed as follows. It front-mixed by stirring a component mechanically until a lump disappears beforehand. This

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mixture was distributed at the rate of 700rpm with the SHIEGUBARI (Szegevari) grinding machine model 01std type with a zirconium-silicate shot of 10-12 meshes. Although usually carried out for at least 1 hour, this grinding process has temperature controlled and can also be performed more for a long time. The obtained trituration mill base was picked out from the grinding machine, deionized water was added, and the last solid content was made 12%.

[0067] The dispersion liquid which described the mill base prescription A were used, and the ink constituent which has the following component was prepared.

Carbon black 4% (weight)

Ternary polymerization object L 1% Polyethylene glycol (molecular weight 400) 10% 1, 3-propanediol 10% Deionized water 75% [0068] The ink constituent was prepared in the following procedure.

(1) Deionized water, PEG and 1, and 3-propanediol was mixed for 20 minutes.

(2) It added into the above-mentioned mixture, stirring the ground mill base (mill base prescription A). Stirring was continued for 20 minutes.

(3) The 20%KOH solution was added and pH of a constituent was adjusted to 8.3.

(4) It filtered by 1.2 micrometer.

[0069] This ink was used by the ink jet printer, and when it printed and examined on six typical kinds of different papers, a good maintenance property, good optical density, and the desirable advanced printing property were shown.

[0070] The ink constituent which has the following component using the mill base prescription B and the process of a publication in the example 2 example 1 was prepared.

Carbon black 3% Ternary polymerization object L 0.75% Polyethylene glycol (molecular weight 400) 14% 1, 3-propanediol 6% Deionized water This ink is used by the ink jet printer 76.25%, and it prints on six typical kinds of different papers. When it examined, good optical density, the good maintenance property, and the desirable advanced printing property were shown.

[0071] The ink constituent which has the following component using the mill base prescription A and the process of a publication in the example 3 example 1 was prepared.

Carbon black 3% Ternary polymerization object L 0.75% Polyethylene glycol (molecular weight 400) 10% 1, 3-propanediol 10% Deionized water When this ink is used by the conventional ink jet printer 76.25%, a good maintenance property is shown, and it is good optical density. The printed matter in which a series of desirable advanced printing properties are shown was obtained.

[0072] The ink constituent which has the following component using the mill base prescription B and the process of a publication in the example 4 example 1 was prepared.

Carbon black 3% Ternary polymerization object L 1% Brand name Liponic EG-1 10% 1, 3-propanediol 10% Deionized water If this ink is used by the conventional ink jet printer 76%, a good maintenance property will be shown and it will print on six kinds of typical papers. When it examined, the outstanding (good optical density is included) printing property was shown.

[0073] The ink constituent which has the following component using the mill base prescription B and the process of a publication in the example 5 example 1 was prepared.

Carbon black 3% Ternary polymerization object L 0.75% 1, 3-propanediol 10% Polyethylene glycol (molecular weight 400) 10% Deionized water If this ink is used by the ink jet printer 76.25%, a good maintenance property will be shown and it will print on six kinds of typical papers. When it examined, good optical density was shown.

[0074] The ink constituent which has the following component using the process of a publication in the example 6 example 1 was prepared.

carbon black (FW18, Degussa AG, the Ridgefield park, N.J.) 3% Ternary polymerization object L 0.75% 1, 3-propanediol 10% Polyethylene glycol (molecular weight 400) 10% Deionized water If this ink is used by the conventional ink jet printer 76.25%, a good maintenance property will be shown and it will print on six kinds of typical papers. When it examined, good optical density was shown.

[0075] The ink constituent which has the following component using the process of a publication in the example 7 example 1 was prepared.

Carbon black (FW18) 3% Ternary polymerization object L 0.75% 1, 3-propanediol 10% Brand name Liponic EG-1 10% Brand name Kathon PFR (a destruction-of-life agent, loam & Haas) 0.15% Deionized water If this ink is used by the conventional ink jet printer 76.10%, a good maintenance property will be shown and it will print on six kinds of typical papers. When it examined, good optical density was shown.

[0076] The ink constituent which has the following component using the process of a publication in the example 8 example 1 was prepared.

Carbon black (SUPESSHARUBURAKKU4A) 3% Ternary polymerization object L 0.75% 1, 4-butanediol 10% Polyethylene glycol (molecular weight 600) 10% n-propanol 0.2% Deionized water If this ink is used by the conventional ink jet printer 75%, a good maintenance property will be shown and it will print on six kinds of typical papers. When it examined, good optical density was shown.

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